COPPER

COPPER

The Science and Technology of the Metal, Its Alloys and Compounds

Prepared under the Editorial Supervision of

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with Chapters by Specialists

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GENERAL INTRODUCTION

American Chemical Society's Series of Chemical Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical progress. The American Chemical Society named as Trustees, to make the necessary arrangements of the publication of the Monographs, Charles L. Parsons, secretary of the Society, Washington, D. C.; the late John E. Teeple, then treasurer of the Society, New York; and the late Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the ACS Series of (a) Scientific and (b) Technological Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successor) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this sketch) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted.

The first Monograph of the Series appeared in 1921. After twenty-three years of experience certain modifications of general policy were indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. By 1944 this differentiation was fast becoming nebulous. Research in private enterprise had grown apace and not a little of it was pursued on the frontiers of knowledge. Furthermore, most workers in the sciences were coming to see the artificiality of the separation. The methods of both groups of workers are the same. They employ the same instrumentalities, and frankly recognize that their objectives are common, namely, the search for new knowledge for the service of man. The officers of the Society therefore combined the two editorial Boards in a single Board of twelve representative members.

Also in the beginning of the Series, it seemed expedient to construe rather broadly the definition of a Monograph. Needs of workers had to be recognized. Consequently among the first hundred Monographs appeared works in the form of treatises covering in some instances rather broad areas. Because such necessary works do not now want for publishers, it is considered advisable to hew more strictly to the line of the Monograph character, which means more complete and critical treatment of relatively restricted areas, and, where a broader field needs coverage, to subdivide it into logical subareas. The prodigious expansion of new knowledge makes such a change desirable.

These Monographs are intended to serve two principal purposes: first, to make available to chemists a thorough treatment of a selected area in form usable by persons working in more or less unrelated fields to the end that they may correlate their own work with a larger area of physical science discipline; second, to stimulate further research in the specific field treated. To implement this purpose the authors of Monographs are expected to give extended references to the literature. Where the literature is of such volume that a complete bibliography is impracticable, the authors are expected to append a list of references critically selected on the basis of their relative importance and significance.

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PREFACE

No fully comprehensive book on copper has been available. It is the purpose of this composite monograph to provide a reference work on all important phases of the subject of copper both as a chemical element and as an industrial metal. It is hoped that the volume will be of interest and value to producers, fabricators, consumers, engineers, research workers, teachers, and others, and that it will afford each group convenient access to knowledge of the other's special interests in this metal. The treatise is aimed to embrace both fundamental principles as applied to copper and the current status of practice in the industry. Some of the less widely known aspects of copper, such as its place in organic chemistry, in biology, and in agronomy, are also treated.

No single author could write a monograph of this scope on so important a metallic element. Even if the volume were confined to metallurgy, the advantages would be obvious of dividing the subject among various authors, each active in or having special knowledge of certain areas. Limitations both of time and of specialized information would prevent any one metallurgist from providing an adequate discussion of the whole field of chemical, physical, and mechanical metallurgy of copper and its alloys.

Division of the subject among so many chapters and authors nevertheless has certain drawbacks. There is no uniformity of style or approach, and there is doubtless a faulty balance. How many readers will say, often with truth, that too small a proportion of the space has been given to this section or too large a share to that?

The editor believed that with authors of the standing of the contributors to this volume the results would be best if each was to cover his subject in his own way, without attempting to meet any prescribed outline or arrangement. Even from the editorial space allotments, necessary to achieve a degree of balance while keeping the length of the book within bounds, there were numerous departures. The editor endeavored as much as possible to avoid inadvertent omissions of important topics that might not appear to fall within the scope of any of the chapter headings, and also to prevent duplication that might result from overlapping. Occasionally some minor repetition of factual matter does appear, but was considered worthwhile for unity and completeness of the chapters in which it occurs.

The purpose has been to treat the whole subject through a planned sequence of original articles, not through a review of the literature on copper. Indeed, the literature of copper is so voluminous that even a carefully selected and restricted general review would be prohibitive. Only a few of the contributors, because of the nature of their individual topics, have advantageously used the review approach in part, but most of the chapters have appended lists of references, in many cases extensive bibliographies.

About 39 per cent of the space in the monograph may be regarded as belonging to the field of occurrence and extractive metallurgy of copper, 16 per cent to the physical and mechanical metallurgy of copper and its alloys, 18 per cent to properties and applications, and 27 per cent to various aspects of the chemistry and physics of copper not included in the foregoing items. Obviously no well-defined separation of the material into these categories is possible, so that this distribution is only general and approximate.

It has been the part of the editor to delineate the monograph in outline, to plan the organization of the material and supervise its presentation, and to ask the various authors to contribute. Their response in these crowded times has been most generous.

A proper acknowledgment of indebtedness would include each of the contributors to the monograph. Some of these specialists have in addition been especially helpful in effort and advice beyond the preparation of their own articles, and other persons who have not been writers of chapters have assisted through suggesting able contributors or by supplying useful information. Acknowledgments by authors appear in several of the chapters, and in addition to these the editor wishes to record his appreciation to the following: Lawrence Addicks, G. L. Bailey, James Boyd, R. M. Burns, G. H. Clamer, T. B. Counselman, D. K. Crampton, J. R. Freeman, Jr., P. T. Gilbert, B. W. Gonser, C. S. Harloff, W. E. Jominy, A. J. Phillips, R. S. Pratt, L. L. Quill, Sidney Rolle, S. Skowronski, H. A. Tobelmann, R. A. Wilkins, and to W. A. Hamor, Editor of the American Chemical Society Monographs.

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COPPER

Chapter 1

The Background of the Copper Industry

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Copper is an exceedingly important metal. For many centuries it has played a notable part in the industrial development of civilization, and the complete exhaustion of our copper deposits would cause a tremendous readjustment in our economic structure. It is not, however, an absolute necessity, as aluminum, silver, and the stainless steels could replace it at a price. In these days of research and specialization traditional uses are on the defensive: hardware is no longer made exclusively of brass, and aluminum is being more widely used in electrical and other fields. Such problems must enter into a discussion of the background of the position of the copper industry today.

An attempt to trace man's use of copper back to its original sources gets out of bounds. Modern archaeology, where geologist, anthropologist, and engineer work as a coordinated team with official government support, is only about 75 years old, but it has pushed the historical horizon back some 6000 years. Beyond that twilight zone history becomes a sort of backward prophecy and some students give copper at least another 2000 years. Generally, articles of hammered copper came first, evidently from sources of native copper; then impure copper castings classifiable as lean bronzes and made from what amounts to a crucible reduction of oxidized copper ores; and finally true bronzes of erratic tin content undoubtedly made by joint reduction of copper and tin ores. There is no surer way to start an argument among archaeologists than to ask where the Near East secured tinstone before the days of the Phoenecian traders, but get it they did.

The classic divisions of time into Stone, Bronze, and Iron Ages carry no uniform date lines. American peoples such as the pre-Columbian Indians, the Aztecs, and the Incas did not possess metals until many centuries later than the Egyptians, and isolated groups such as Captain Cook discovered in his Pacific voyages can still be found living in the

Neolithic Age. Nor is the order of the metals fixed: parts of Africa start with iron, and North America, having virtually no tin, had plenty of pure copper but no bronze. In very broad terms the oldest civilizations had bronze in general use (as distinguished from tomb relics) in about 2500 B.C. and iron in 1000 B.C., neglecting the negligible amounts of meteoric iron discovered in very early times. Recorders vary greatly in their chronology, and the end is not yet.

The earliest exhumations yield artifacts of gold, silver, and copper. These, again neglecting meteoric iron, are the only common metallic elements often found "native" in nature. All three were used for ornament, but copper alone was found suitable for weapons, tools and utensils. The ores of copper are very widely distributed—indeed copper is considered one of the "trace" elements necessary to life—and native copper is found in mineral outcrops in many parts of the world, usually in a high degree of purity (witness the market premium which Lake copper from Michigan commanded for many years). Early knives, etc., are almost always of unalloyed copper which had been work-hardened by hammering in the cold. Pure copper is so malleable that it can be beaten to a fine edge without cracking; it was thus hardened to such a degree that it was even suggested that the Egyptians had some secret tempering process now lost. If it is objected that native copper is not now found in a given region, we must remember that mines are subject to depletion and that the tonnages involved are minute by present-day standards. As far as we can now guess, all the copper mined in the world up to 1800 A.D. would not supply the demand of any recent single year. No doubt the problem of circulating secondary copper existed then as today.

Cast copper soon appears and doubtless gave the artisans a rough time. With molten copper's avidity for oxygen, sound castings are not to be made by amateurs even today. But the ancient picture changed with heat. Nearly all articles became made of a sort of bronze, resulting from the reduction of the local oxidized ores, doubtless at first accidentally in accordance with the camp-fire theories advanced to account for various metallurgical "firsts".

Almost anything added to pure copper which it will accept in solid solution will increase its hardness, and the simple reduction of an impure copper ore with charcoal will yield a sound casting of an alloy workable within limits. Sometimes the predominating impurity is arsenic (Egypt, Ireland), sometimes antimony (Hungary), tin (Britain), or nickel (Germany). Then begin to appear alloys that contain so much tin that deliberate mixtures of ore are evident. Sometimes copper plus tin add up so nearly to 100 per cent, notably in the case of the early Inca bronzes of South America, that native copper and pure tinstone must have been available. In Roman times even impure brasses are common although zinc as an element was not identified for another 1500 years.

Bronze can also be work-hardened, and with it a tool can be made much stronger than of copper, although without quite as keen an edge due to lessened malleability. No early appreciation seems to have developed among the founders and smiths as to the effect of varying amounts of tin upon the malleability so desirable for forging, or upon fluidity for casting, but in time a metal approximately 90 copper-10 tin was used for casting works of art. This alloy corresponds to modern gun metal, and is essentially the statuary bronze of today except that about 3 per cent zinc and occasionally some lead replace the equivalent tin, giving better definition and lowering the cost of the alloy.

However primitive the smelting operations remained for centuries, the early metal workers developed amazing skill in handling the product. The repoussé work with copper and the art casting of bronze in Greece have never been surpassed. The Statue of Liberty in New York Harbor was made, just as was the Colossus of Rhodes, by hammering copper sheets from the back into wooden molds, riveting these sections together and stiffening with internal stays. The "lost-wax" process for casting was also devised very early. A rough fireproof core was built up and coated with wax which was then carved by the sculptor. Successive coats of grout were smeared on this until a sufficiently thick mold was obtained and necessary ports and gates were provided. When molten bronze was poured in, the wax ran out and a thin hollow casting of fine detail resulted after breaking away the mold. Today this process has wide application under the name of "precision investment casting" for turbine blades, etc., low-melting alloys often being substituted for the wax.

On the smelting side progress was almost unbelievably slow. The early furnaces were simply shallow pits where oxidized ores were heated with charcoal, forming cakes of crude metal. It seems to have required centuries to arrive at the idea of forced blast, first by blowpipes, then bellows, and finally arranging to utilize the prevailing winds by building on sloping ground. In fact such rudimentary blast furnaces were found in operation in Japan after the country was opened to the world by Commodore Perry's historic visit. Here again primitive smelting was joined to superb craftsmanship in the use of the bronze produced. Much work had been done on unusual alloy compositions, pickling solutions to get patinas, and layer effects using alloys of different colors, producing unique articles of the highest artistic rank.

Egypt can claim most of the credit for such metallurgical development as there was in very early times, and here we meet the occult influence of magic and priestly secrets which carried forward into the days of alchemy. Legend has it that wayward angels on their earthly carousals divulged supernatural knowledge to favored mortals. The idea of secrecy regarding special knowledge passed through many stages involving chemistry, metallurgy, and medicine, including the priestly magic of Roman and medieval times. We have vestiges of it today in the Rosicrucians, and even 50 years ago many chemical and metallurgical plants were quite inaccessible to the outside world, although hardly run by astrologists nor aware of their traditional ancestry.

Classic literature sheds very little light on metallurgy apart from the fact that so many of the writings have been lost. Occasionally someone like Pliny undertakes to deal with it in the course of trying to write an encyclopedia, but unfortunately has very little idea of what he is talking about. The scientific dicta of Aristotle seem to have had almost scriptural authority for 1500 years after his death. He considered different forms of matter to be the result of the interaction of elemental earth, air, fire, and water, plus a mystic influence (pneuma). Many ingenious explanations of metallurgical phenomena came out of this, but such speculations could hardly contribute much to practice.

After the fall of the Roman Empire the Arabians took over and Baghdad became the center of scientific learning. Arabic translations of Aristotle appeared and Geber (Jabir), the most famous chemist of his time (800 A.D.) and a great student of Aristotle, believed that all metals were impure forms of gold, the perfect metal, and that the key to transmutation lay in understanding how to combine mercury, salt, and sulfur in the proper way.

Metallurgy and medicine ran parallel courses. Early work in Egypt and priestly magic, the rating of Galen in the second century A.D. as an authority lasting for more than a thousand years, the translation of his works by the Arabians in the Dark Ages, the postulating of his four "humors" and the search for an elixir of life gave the alchemists a double goal. Poverty and disease have always been kin, and gold and panaceas seemed natural associates. In a way the ideas of unity of matter and elixirs seem less laughable than they once did in the light of atomic fission and today's antibiotic drugs, and the alchemists may be justly considered the first scientific researchers. However, while the Arabians kept the light burning during the Dark Ages, Baghdad was not a mining center and medicine not a happy partner for metallurgy. Europe remained in darkness and the universal brigandage caused the suspension of all copper mining operations.

This unfruitful and nearly unrecorded state of affairs continued until Roger Bacon, who died in 1294, made a plea for breaking away from Aristotelian speculation and studying nature by experimentation. Unfortunately his brilliant scientific work was largely confined to physics, and beyond some minor monkish records of that time not much is recorded in metallurgy. Two hundred and fifty years later, a complete industry, developed wholly empirically, is disclosed in Germany, particularly through the "De Re Metallica" of Agricola, himself a physician by the way, who, thanks to the Hoovers, gives us in English a clear description of copper concentration, roasting, matting, reduction, and refining. The operations were on a tiny scale, to be sure, with many successive treatments and time no object, but the processes were all there substantially as we use them today. About this time the famous Mansfeld smelter in Germany and the Swansea smelter in Wales started operations.

Another smelting center was Sweden—today we still hear of Swedish iron and Swedish copper for special uses—and nearly 200 years later in "De Cupro" Swedenborg brings things up to date, but with little evident further progress and still with the secret formula flavor, such as preparing a reagent from crab's eyes—and this in the early days of George Washington! The output is still tiny, something like 9000 short tons of copper world production in 1750, little more than now produced in a single day.

So we reach the beginning of the nineteenth century with copper metallurgy on a rational working basis just as the Industrial Revolution comes into being with powder for blasting and power for pumping and hoisting. We leave a period of some thousands of years during which science was all hypotheses and no facts, industry all facts but no understanding, and time a matter of no consequence. We enter an era where time seems out of all proportion in the scheme of things and scientific research has left practice breathless. Europe now becomes the center of the copper industry, the ores coming from the Mansfeld and adjacent areas of Germany, the rich mines of Cornwall and Devon in England, oxidized ores from South America, and the great pyrites deposits of Spain and Portugal.

The Mansfeld and Welsh processes for treating copper ores, stemming from Agricola's time, have now become standard practice. Both involved a series of oxidations and reductions for the elimination of sulfur but differed in their individual adaptation to their supply of ore. The German ores were lean in copper, carried considerable values in silver, and were not accessible to cheap fuel. Heap roasting and blast-furnace reduction were therefore used, with a final step involving pulverizing white metal, dead roasting it, extracting the silver sulfate with water, and subsequent reduction of the copper.

The Welsh process was developed to a fine art. Here white metal was produced by a series of partial roastings and meltings but the operations were on small reverberatory hearths and at a high fuel cost. This sounds simple, but judgment and skill are required to get just the right oxidation and grade of matte to secure maximum elimination of arsenic and minimum loss of copper in the slag. The white metal was subjected to successive steps of melting in an oxidizing atmosphere, skimming slag formed by the reaction of ferrous oxide with the siliceous hearth, chilling, remelting after the surface crust had oxidized, and so on. It will be seen that all the elements of an acid-lined converter are here except the means of getting oxygen into rapid contact with the body of the copper.

When about ten per cent of the copper had been reduced, this was withdrawn; it contained most of the gold and a substantial proportion of the silver and impurities. The fine copper eventually obtained from the remaining charge was correspondingly purer than the average and became the famous "Best" or later "Best Selected" of a hundred years ago.

A great foreign trade was built up with British ships carrying coal out and returning with cargoes of ore, and Britain for many years was the headquarters of the copper industry. In fact by 1860 Swansea was smelting 90 per cent of the world output and most of the copper matte produced in the United States before the development of the copper converter was shipped to Wales for treatment.

By mid-century Spain and Portugal forged to the front with their great deposits of massive pyrites for making sulfuric acid. About 1860, with the development of the Henderson process for extracting the copper and other values from the resulting cinder, this area became a major source of copper for the next 50 years. The Henderson process comprised a salt roast, followed by leaching and fractional cementation of the nonferrous metal values, leaving the residue as an iron oxide for steel manufacture. The success of the process formed a background for many chloride leaching schemes in later years.

Until well into the nineteenth century, while Chile was becoming an important producer of copper, the United States was a negligible factor, although some minor custom smelting was done on imported ores. The reason was very simple—the country as then developed had no major deposits of copper worth mentioning. Even today the only significant Eastern mines are those of the Ducktown area in Tennessee. The situation changed overnight with the discovery of the enormous deposits of native copper near Lake Superior about 1845. Much of this copper needed only melting to produce the Lake copper which became the standard of copper purity for over 50 years. In fact it took years for electrolytic copper, even after large-scale production began, to shake off the premium Lake copper enjoyed in the market. So strong was the trade prejudice that copper produced electrolytically from some of the less pure Lake mineral still sold at the Lake premium.

The nucleus of the large copper installations at Baltimore came into being about the same time as the copper discoveries in Michigan. Smelting was along Swansea lines and Cuba and Chile were the principal sources of ore. The Revere Copper Smelting Works in Boston Harbor also started a copper blast furnace. From then on, except for the upheaval of the Civil War, the American copper industry grew rapidly on its way to the giant of today. The large deposits discovered at Ducktown, Tennessee, resulted in all sorts of experimentation with different types of furnaces in the 1850's. In the 1860's active mining in Arizona commenced, but the transportation problems were very serious before the railroads entered this territory. In the 1870's some ore was shipped from Montana. In the 1880's the Orford smelter became the first of a series of copper plants near New York Harbor, and Arizona started the production of large quantities of black copper by mixing oxide ores with unroasted sulfides in blast furnaces. By this time Montana was shipping 60 per cent matte to Swansea, the copper converter was being tried out in Butte, and electrolytic refining was on an experimental basis. The railroads were spreading to the mining districts: Butte was reached in 1882.

In the 1890's the electrolytic refineries were fully developed, producing fine copper the equal of Lake; America freed herself of European tethers, and has become the largest copper producer in the world, after having started in 1845 with a total output of 112 tons. While the basic processes were derived from Europe, the great developments in practice are American. Wet processes have not been discussed here, since, except for the Rio Tinto leaching of pyrites, the early work in Europe and much of the salt roasting schemes in America are mostly obsolete. The newer sulfate leaching of oxidized copper ores and the great changes in copper smelting practice brought about by flotation and giant reverberatories will be taken up in detail in later chapters of this book.

The discussion of the growth of the copper industry now brings us into the realm of statistics. The handling of statistics calls for asbestos mittens, and copper affords no exception to the rule. It is only in recent times that consistent and comprehensive compilations have become available, and the further we reach beyond such simple quantities as production and prices in the better-known countries, the shorter becomes the period. Secondary copper cycles, inventory stocks, government duties and subsidies, cartel speculations, the varying purchasing power of money, and even confusion between long, short, and metric tons all help to confound matters. In the graphs presented, individual points represent the average annual short tons per decade, thereby smoothing out abnormal fluctuations and canceling out inventory stocks so as to give a better perspective as to long-term trends. It also enables some arbitrary assumptions to be made in filling gaps in information without unreasonable distortion of the facts.

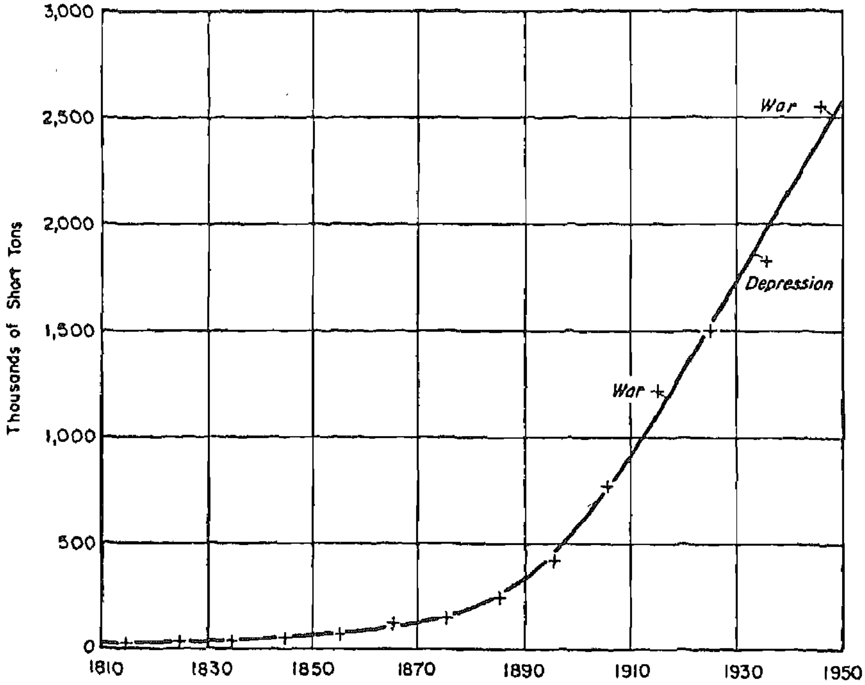

FIGURE 1-1. World output of copper, average annual short tons per decade.

The world output for the last 150 years is shown in Figure 1-1. The steadiness of the upward trend is remarkable, and if the total continues along this curve it is hard to see where the copper is going to be found. Government estimates of the world's copper ore reserves indicate that the present rate of consumption would result in complete exhaustion in about 45 years, or if the curve presented in Figure 1-1 continues as indicated, perhaps 25 years. The mining industry is made up of individual producing mines, each of which grows rapidly in output after an initial period and then subsides more slowly into exhaustion after the peak is passed. Figure 1-2 gives the history of the Lake Superior district as shown by the statistics of output for the State of Michigan. This same curve can be used to typify the industry as a whole except that we are now probably close to the peak with the future depending upon the rate at which new deposits may be found. Current opinion seems to be that the great copper deposits of the world have already been found; but, on the other hand, while there may be no literally unexplored areas left on the globe, a number are but very superficially known. It is true that the days of the old-time prospector and his "strikes" based on mineral outcrops are over, but instead we have geophysics with airplane observation

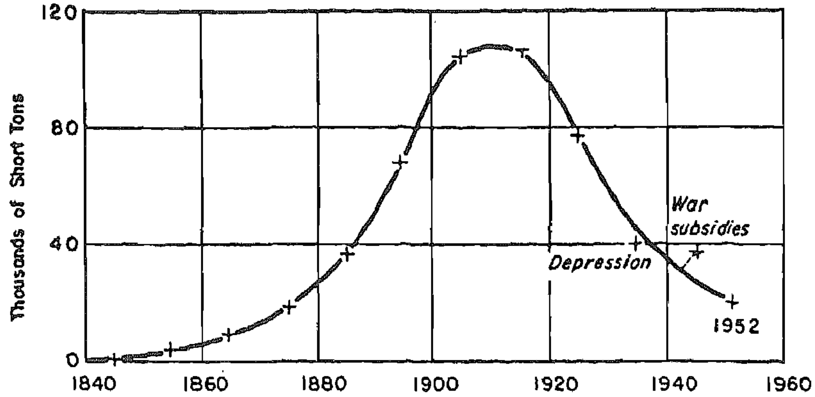

FIGURE 1-2. Copper output of the State of Michigan, average annual short tons per decade.

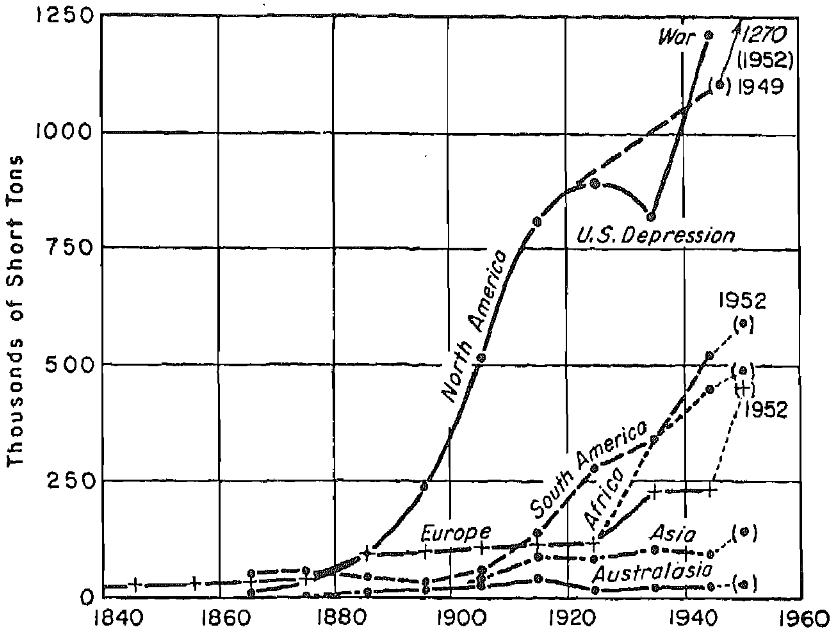

FIGURE 1-3. World copper production by continents, average annual short tons per decade.

and geochemistry with the study of vegetation still in their infancy. Who knows?

In Figure 1-3 is shown the distribution of the copper mined in the several continents. It is apparent at once that the Americas and Africa have the future in their hands. Australia is a negligible contributor and Asia has practically only Japan; Europe does include Russia, the main European producer at present, with large known copper reserves and for a period in the 1700's, before England and Chile got into their stride, the world's largest producer. This distribution is more interesting when shown in term of percentages of the total as is done in Figure 1-4. Europe was the master until 1840 and shared with South America the command until 1860, while from 1890 on North America took over.

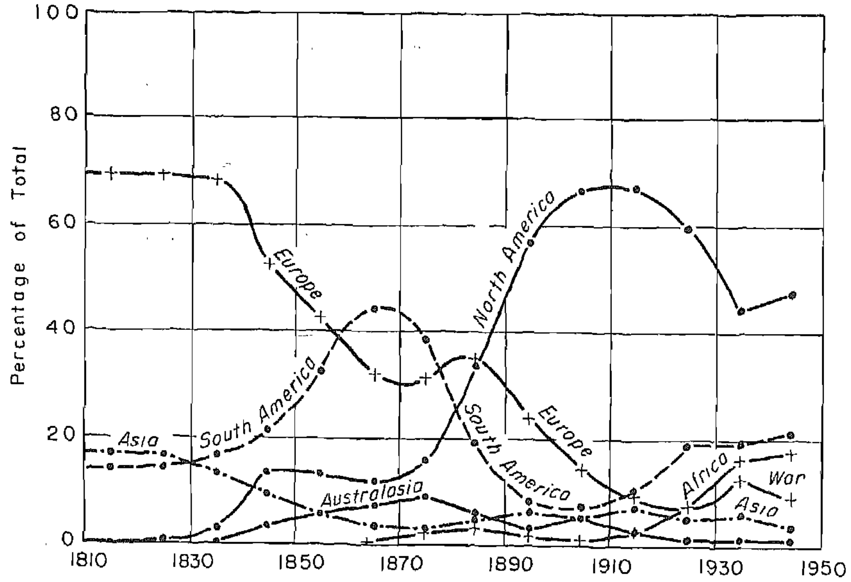

FIGURE 1-4. Percentage distribution of world copper production by continents.

In Figure 1-5 the contribution of the United States is shown both in tons and in percentage of the world output. These curves show clearly that this country has reached the foreseeable zenith of copper production and has lost its impressive domination over all other sources of supply. The situation is better than it looks, however, when it is considered that American capital controls nearly all of the Latin American mines and has a very substantial minority share in British interests in Canada and South Africa. Certainly the English-speaking peoples control three-quarters of the world's copper mines.

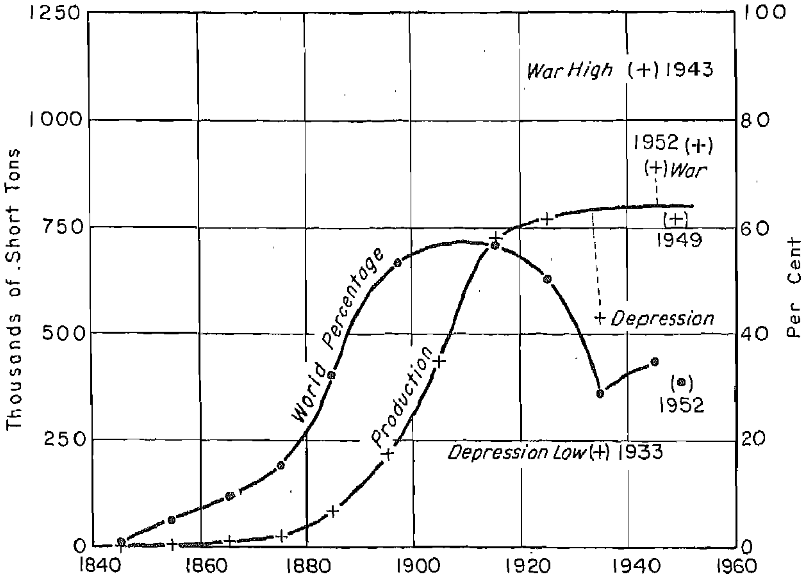

FIGURE 1-5. Copper production of the United States, average annual short tons per decade.

In the early 1800's Swansea was the copper center of the world, the smelters purchasing incoming ore cargoes at auction and the Smelters Association establishing the price of the copper produced. As Chile gradually took the position of leading producer and saw the large profits obtained at Swansea, the Chileans built charcoal blast furnaces to make black copper from their rich oxidized ores and "Chili Bars", running from 95 to 99 per cent copper and often containing precious metal values, were quoted on the English market for the balance of the century.

As the importance of Swansea diminished, Liverpool and finally London became the quotational center, and about 1870 the imaginary material, "Standard Copper", of variable definition at different periods, came into use as a market yardstick on which to base contracts, subject to a schedule of premiums and penalties for the quality of copper delivered. "G.M.B.'s" were good merchantable brands accepted for trading on the London Metal Exchange. "Best Selected", already described, ran around 99.75 per cent copper content and was long popular with the British brass trade. "Tough Copper," for which there are quotational statistics throughout the whole nineteenth century, ran 99.2 to 99.5 per cent copper.

The great increase in American production and the high electrical conductivity, first of Lake and then of electrolytic copper, gradually transferred the copper center to New York where it still remains. For a few years after 1900 Lake still commanded a considerable premium over electrolytic, due partly to tradition and partly to the rather uncertain quality of the first electrolytic copper produced; but this soon dwindled although it has never absolutely vanished.

In New York, quotations are published f.o.b. Atlantic seaboard refineries, although sales are actually made on a delivered basis. They are net for electrolytic wirebars and ingot bars and a schedule of premiums is applied for other shapes and an allowance made for cathode shipments. Fire-refined and secondary copper are subject to contractual allowances but naturally bear a close relation to the electrolytic quotation. In England, where much progress has been made in developing fire refining due to the low silver and gold values in the British African coppers, there is now a London quotation for "electrolytic and high-conductivity fire-refined" copper with a schedule of deductions for other grades of fire-refined.

The average price of copper per decade during the last 150 years is shown in Figure 1-6. It is hard to get comparable quotations over such a long period, as the quality of the copper delivered improved so with time. In constructing the curve the English quotation for Tough Copper is used for the first hundred years and the New York quotation for electrolytic thereafter.

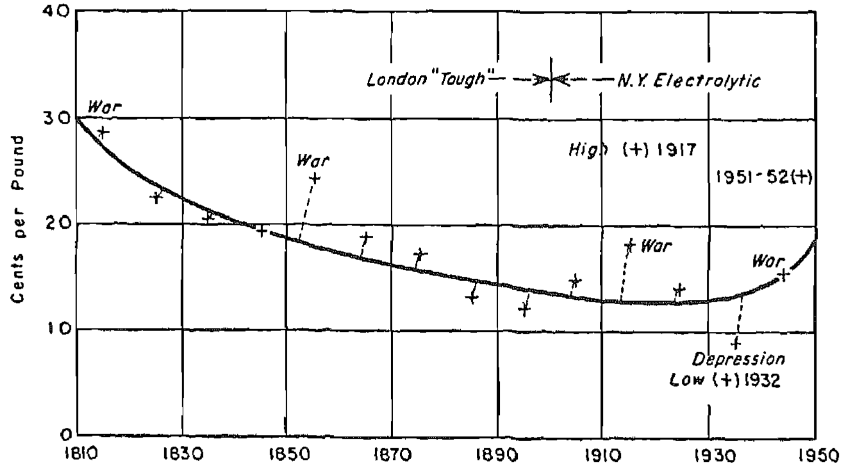

FIGURE 1-6. The price of copper since 1810.

The price of copper may be said never to be satisfactory for long at a time. The quotation often varies excessively within the 10-year periods used for points in the graphs. The producer is generally dealing with a feast or a famine and the independent consumer has his difficulties with any long-range program. At low prices the high-cost mines operate at a loss, and peak prices always injure the industry because the consumer turns to substitutes and sometimes does not return to copper when prices drop—for instance shoe eyelets were once made of brass but are now of steel. The price structure is also affected by the difficulty in meeting fluctuating demand of business cycles. Copper is too expensive a material to stock in large quantities in refined form. It can, however, be stored in the ground without carrying charges; therefore when sales fall off some mines close down. As starting up a mine with its equivalent smelting capacity is an expensive operation, it is not done until the market obviously justifies it and then it takes several months for its output to reach the market and by that time a scarcity is probably developing.

Another oddity is that copper can be produced more cheaply when the demand is low than when it is high. Obviously the cost of producing copper depends primarily on the richness of the ore, and there is a great spread in costs between different mines. The market, when free of artificial interference, is therefore determined by the cost at the poorest mine which can be profitably operated in order to satisfy the gross tonnage demand. As demand drops the average cost of production drops, although at the same time the ore reserves are curtailed by lower mining cut-off values at all mines. In a few instances associated metals carry the burden—in part of the Canadian production copper may be considered as a by-product of nickel and South America has offered examples of copper as a by-product of silver—but most of the great copper deposits of the world have comparatively small associated values. In late years the net yield of all copper ores produced in the United States has been below one per cent of copper and below 30 cents a ton in gold and silver.

A discussion of price would not be complete without considering the purchasing power of the dollar. Various commentators have pointed out that copper should be judged in contemporary values. It is hard to get a fair yardstick because the standard of living in the various countries where copper is produced and the changing costs of transportation from once inaccessible locations enter into the picture. If we take the U. S. Department of Labor Index for a group of wholesale commodity prices and the price received by United States producers for their output (remembering, however, that before 1900 much of this output was crude material exported to Swansea for treatment) we may barter a basket of groceries for a copper ingot as shown in Figure 1-7, thereby indicating that copper has reflected the great technological advances in a corresponding lowering in price.

In Figure 1-8 an attempt has been made to show where copper is consumed. The United States and Europe are naturally the great fabricating centers and the effect of World War II in devastating Europe

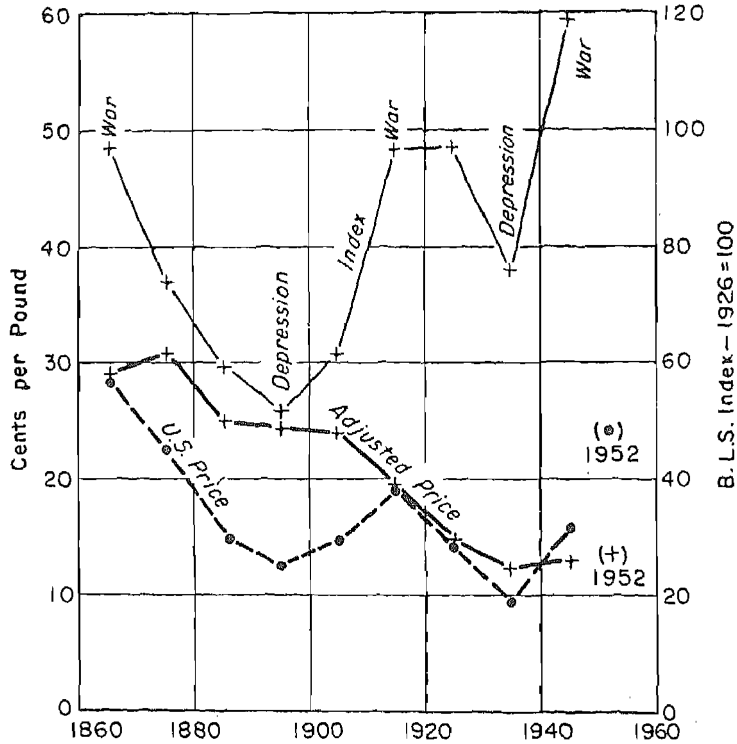

FIGURE 1-7. Price of copper in the United States, price adjusted to the cost of living, and price index.

while calling upon America is interestingly illustrated. Statistics covering consumption are limited and not too satisfactory in war periods, but the general picture is probably fair. World consumption is taken as identical with world production and in 10-year periods this must be so. While areas other than the United States and Europe are obtained by difference and cannot be analyzed beyond noting that Canada and Japan are included, their contribution may be seen to be material. We sometimes congratulate ourselves that America contains both the principal copper supply and the chief manufacturing demand but we overlook the fact that the cost of transportation between the Rocky Mountains and the Atlantic seaboard will pay a lot of ocean freight between say Africa and England.

The shrinkage in American production coupled with the great demand for fabrication has naturally resulted in changing the United States from an exporting to an importing country and this is illustrated in Figure 1-9, constructed by merely contrasting the production in Figure 1-5 with the consumption in Figure 1-8.

All statistical studies are complicated by the run-around of copper scrap. Except in minor uses such as in fungicides and salts and in excep-

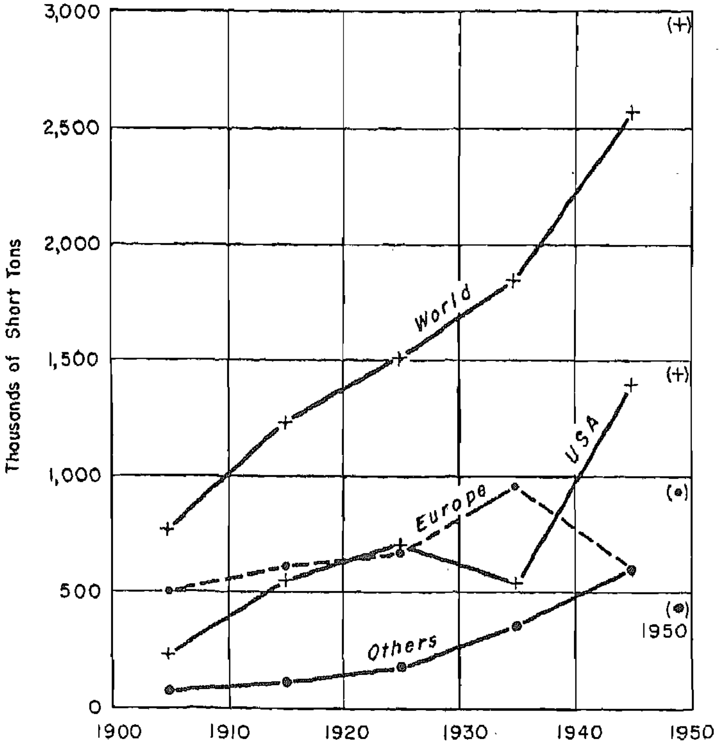

FIGURE 1-8. Approximate consumption of copper, average annual short tons per decade.

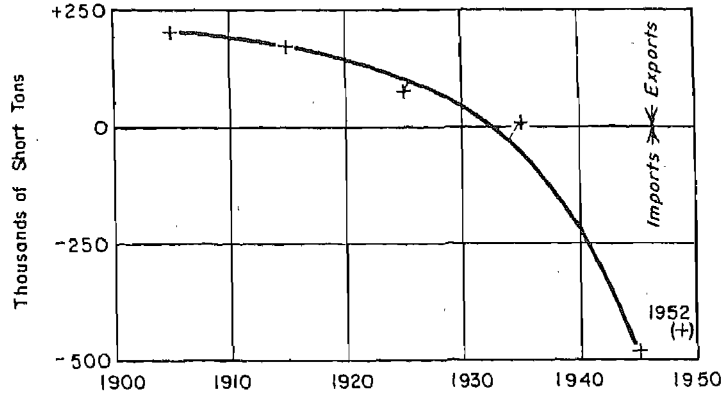

FIGURE 1-9. Approximate copper export-import balance in the United States, average annual short tons per decade.

tional locations as in acid soils, copper is subject, at least theoretically, to a very high reclamation value, and as installations involving copper are modernized great quantities of scrap come upon the market. Even warfare leaves its empty cartridge cases. So-called primary scrap such as bad castings or punched strip have no bearing on the industry, but they do enter the statistical picture because refining and fabrication are seldom within the same fence. Secondary scrap, which comprises everything from a worn-out electric motor to hurricane damage and discarded brass, bronze, or what have you, comes on the market arbitrarily and is quite out of control of the virgin-copper producer who simply has to adjust his output to the remaining demand. While much old brass or bronze is remelted to new brass or bronze ingot, much unclassified scrap emerges as electrolytic copper. The tonnage of copper circulating in secondary material is very large; taking round figures in the United States today, including primary and secondary material of all types, it is of the order of 70 per cent of the virgin copper consumed; of this amount a little more than half is in the form of "old scrap" competing with new supply.

Sufficient statistics do not exist to enable long-term graphic analysis of this picture and in any event there is no logical relation between momentary supply of virgin copper and that of secondary copper. In general, however, it is evident that circulating material is becoming a larger factor as the years go by; probably the great improvement in methods of recovery and more rapid obsolescence in these days of high-pressure living have much to do with it. Any substitution of aluminum or other material for a traditional use of copper would correspondingly displace virgin copper.

In the earliest times copper was used for ornament and utensils, but it must have been so scarce that only palace households could afford it. Armaments surely had much to do with its development as war seems to have always been mankind's principal preoccupation, and the have's and have-not's existed then as now. Bronze weapons were much better than stone clubs and slings and their possessors prospered accordingly. The advent of iron changed this—the iron armament of the Romans is supposed to have facilitated the subjection of their bronze-accoutered adversaries. Strangely the golden age of art-bronze also seemed to fade with the advent of iron, and the use of copper shows no great strides for a long period thereafter.

The use of a metal is closely associated with its natural properties. Copper, aside from its ornamental value as a red metal, is outstanding in its ability to form simple useful alloys, its resistance to chemical corrosion, and its high conductivity for heat and electricity. Art, weapons, tools, and cooking utensils were natural uses. When we come down to a hundred and fifty years ago, there developed a great demand for copper sheet for roofing and especially for plating the bottoms of wooden sailing vessels, to restrain the growth of barnacles in the clipper-ship era when fortunes depended on the speed of long voyages. It was this demand which brought about the early American ventures in copper smelting and rolling. Nevertheless it was the brass and bronze trade that formed the backbone of the copper industry, and this prospered enormously in England with the development of railroads and machinery in the early nineteenth century.

Then came the electrical era of the dynamo, which replaced primary batteries, and of the electric light. The former gave a source of electric energy which in the development of copper refining by electrolysis made possible the transformation of impure copper into the high-conductivity material that the electrical industry needed for its development. Today copper may be roughly stated to go 50 per cent to the wire mills, 45 per cent to the brass mills, and 5 per cent to miscellaneous uses. An analysis of end uses leads again to the conclusion that at least half of the consumption goes into channels where electrical conductivity is the controlling factor, a significant amount into items like automobile radiators where heat conductivity is important, and most of the balance into buildings, machinery, etc.

This survey may well conclude with a brief look at the competitive position of aluminum, which from a laboratory curiosity 70 years ago has become one of the high-tonnage metal group. The world production has now reached half that of copper and the price has fallen rapidly, equalling that of copper for the last decade and well below it at the moment of writing. Aluminum is one of the most plentiful of the elements and theoretically everyone has a mine in the clay of his own backyard. The catch is that electrolytic reduction requires nearly pure alumina; high-grade bauxite deposits are not only uncommon but have a way of turning up in localities far from suitable sources of the power so necessary for reduction. It takes some 25,000 kw-hr to produce a ton of aluminum electrolytically and a moment's figuring will show that at the lowest of the power costs at the great government dams and other centers power is going to account for several cents a pound in the cost of aluminum. The cost of transporting bauxite long distances or of purifying high-silica material creates another floor under the price level so that it is idle to expect the price curve to go surging down indefinitely. At a price, however, it can be truly said that the supply is unlimited.

One or two popular misconceptions regarding the comparative values of copper and aluminum need clearing up. For instance it is usual in tables of properties to find the electrical conductivity of aluminum rated at 63 per cent of that of copper. This figure is based on the comparative resistance to an electric current across a centimeter cube, a volume, while the market price is per pound, a mass. When a price comparison is made of the cost of carrying current at a given loss, the specific gravity as well as the effects of commercial impurities and of hard drawing must be taken into account and it will then be found that one pound of aluminum is roughly the equivalent of two of copper.

Aluminum has already taken over many power transmission installations and would enter much more largely into industrial wiring were it as easily soldered as copper.

A pound of aluminum is 3.3 times as bulky as one of copper, but for equal conductivity only about 1.6 times. The extra volume may be a disadvantage where switchboards are limited as to bus-bar space, or an advantage in power lines where conductors of larger diameter suffer less corona loss. Where these factors do not enter, as say in architectural trim, aluminum alloys have great price advantage. When it is discovered how to make an easy, permanent electrical joint in the field and how to apply electroplate and enamel finishes as easily as to copper and brass—and much progress is being made along these lines—copper will have an even more formidable competitor.

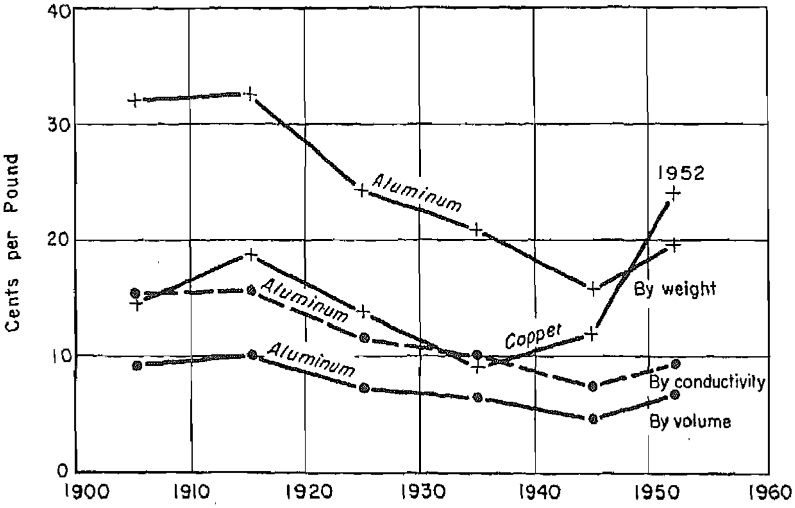

FIGURE 1-10. Cost of copper vs. cost of aluminum.

With these things in mind Figure 1-10 has been drawn to show a triple comparison between the costs of copper and aluminum on a pound basis, on an equivalent electrical conductivity basis, and on a volume basis.

The point of it all is that the copper industry is increasingly going to have to reckon with aluminum as an encroacher on fields it has long, perhaps too complacently, considered its own.

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Chapter 2

Copper Minerals, Ores, and Ore Deposits

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Copper minerals are naturally occurring chemical compounds of crystalline structure, among which the native metal is also included.

Copper ores are natural mixtures of copper-bearing minerals and copper-free minerals, in which mixture copper is sufficiently abundant and occurs in such manner that it can be mined and extracted at a profit.

Bodies of copper ore found in the earth's crust constitute ore deposits, and individual deposits range in size from a few thousand tons to over a billion tons. These ore deposits may be confined to very near the earth's surface, or they may extend to known depths of several thousand feet.

Copper ore bodies are unusual and exceptional concentrations in the earth's crust and occupy only an exceedingly small fraction of the rock formations with which we are familiar. Thus they are "freaks of nature" whose origin is brought about by special geologic processes.

Deposits of copper are widely distributed, both geographically and geologically. Geologically such ore bodies are found in a variety of host rocks under greatly varied structural conditions. As regards the period of their formation, the range extends from the Precambrian to the Tertiary, embracing most of known geologic time. Throughout this profoundly long interval, the same copper compounds have been deposited in rocks that have undergone chemical changes of recurring similar habit.

COPPER MINERALS

Although some 165 copper minerals are known, those commonly found in ore deposits are relatively few in number. These are listed in Table 2-1.

In this listing, three important groups of copper-bearing minerals are included. The first is that of the "primary" or "hypogene" minerals, or those deposited at considerable depth in the earth by processes related to igneous activity. Examples of these are bornite, chalcopyrite, enargite,

TABLE 2-1. COPPER ORE MINERALS

Mineral	Composition	Per Cent Copper	Color	Luster	Hardness	Specific Gravity
Sulfides						
Bornite	Cu_5FeS_4	63.3	Between copper-red & pinchbeck-brown	Metallic	3	5.06-5.08
Chalcopyrite	$CuFeS_2$	34.5	Brass-yellow	Metallic	3.5-4	4.1-4.3
Enargite	$Cu_3(As,Sb)S_4$	48.3	Grayish-black to iron-black	Metallic	3	4.43-4.45
Tetrahedrite	$Cu_{12}Sb_4S_{13}$	45.8	Flint-gray to iron-black	Metallic (splendent)	3-4.5	4.6
Tennantite	$Cu_{12}As_4S_{13}$	51.6	Blackish lead-gray to iron-black	Metallic (splendent)	3-4.5	4.37-4.49
Chalcocite	Cu_2S	79.8	Blackish lead-gray	Metallic	2.5-3	5.5-5.8
Covellite	CuS	66.4	Indigo-blue or darker	Submetallic to resinous	1.5-2	4.6-4.76
Complex						
Famatinite	$Cu_3(Sb,As)S_4$	43.3-47.9	Gray with tinge of copper-red	Metallic	3.5	4.52
Bournonite	$PbCuSbS_3$	13.0	Steel-gray	Metallic (brilliant)	2.5-3	5.8-5.9
Oxides						
Cuprite	Cu_2O	88.8	Red	Adamantine to earthy	3.5-4	6.14
Tenorite	CuO	79.9	Gray to black	Metallic	3.5	5.8-6.4
Malachite	$CuCO_3Cu(OH)_2$	57.3	Bright green	Adamantine to earthy	3.5-4	3.9-4.03
Azurite	$2CuCO_3Cu(OH)_2$	55.1	Azure-blue	Vitreous, almost adamantine	3.5-4	3.77-3.89
Antlerite	$Cu_3SO_4(OH)_4$	54.0	Green	Vitreous	3.5-4	3.9
Brochantite	$Cu_4SO_4(OH)_6$	56.2	Green	Vitreous	3.5-4	3.9
Atacamite	$Cu_2Cl(OH)_3$	59.5	Green	Adamantine to vitreous	3-3.5	3.76-3.78
Chrysocolla	$CuSiO_3.2H_2O$	36.0	Green to blue	Vitreous to earthy	2-4	2.0-2.4
Native						
Native copper	Cu	100.0	Copper-red	Metallic	2.5-3	8.95

etc. The few examples of complex minerals listed are also primary, but minerals of this type are not abundant in economic deposits.

The second group is composed of the "oxidized copper minerals," or those commonly formed by weathering of copper sulfides exposed by erosion. Such minerals as atacamite, malachite, azurite, chrysocolla, and brochantite belong to this category.

The third group is that of the so-called "secondary" or "supergene" sulfides. These minerals are generally formed by copper leached from sulfides exposed near the earth's surface, the copper being carried downward to where it is precipitated near water level. The simple sulfides, chalcocite and covellite, are members of this group, although not exclusively so, and other copper-bearing sulfides are occasionally placed in this category.

Native copper is commonly found in the oxidized zone; in contrast to this usual occurrence, the great native copper deposits of Michigan are now believed to be of hypogene origin.

Copper Ores

Copper ores vary as regards type (whether sulfide or oxide), in the valuable metals occurring in them, in their tenor, in the kind of associated gangue minerals present, and in texture and hardness.

Copper ores are commonly distinguished as "oxidized ores" or "sulfide ores" and may range between "high grade" and "low grade," the latter designation roughly expressing the copper content.

A sulfide copper ore is a natural mixture containing (1) copper-bearing sulfide minerals and (2) associated "gangue" minerals that are either valueless, as regards their metal content, or of subordinate importance for some other purpose. The gangue may consist simply of the minerals making up the host rock, or it may be composed of various other minerals developed during the general ore-forming process, or it may occur as a combination of these two groups. Thus the gangue might consist of a sulfide, such as pyrite, along with quartz, sericite, calcite, barite, etc. From an ore like this, in addition to the principal value in copper, pyrite might be reclaimed as a by-product for its sulfur, and barite might be recovered to be used in well-drilling.

An oxidized copper ore is similarly a natural mixture of oxidized copper minerals and gangue. Examples would be malachite and azurite in dolomite stained by iron oxide, or brochantite and chrysocolla deposited among the silicates that compose a noritic rock.

Thus, there are various sorts of copper-bearing ores treated commercially, and part of the value derived from an ore may come from other metals associated with copper or from other "nonmetalliferous" constituents. It is seldom that some other product does not contribute something to the value of a copper ore.

There are many ores in which copper is dominant and is the principal metal recovered. Commonly associated with this copper are minor amounts of gold and silver. Molybdenum is also occasionally recovered in some plants, and very minor amounts of the platinum metals may be present to be extracted in refining. Nickel, likewise, may occur in certain kinds of copper ore, and cobalt is a valuable associate of copper in the Belgian Congo. Mineralogically, such a sulfide ore might contain, for example, chalcocite and pyrite dispersed through a gangue of sericite schist; or chalcocite, chalcopyrite, and pyrite with a little molybdenite might be associated with gangue minerals derived from the alteration of quartz monzonite rock.

In some ores, copper occurs in coordinate importance with other valuable metals to form a so-called "complex ore." Skillful beneficiation, for example, might seek to recover lead, zinc, and copper from such material. The sulfide minerals in this kind of ore might be galena (PbS), sphalerite (ZnS), chalcopyrite, and pyrite contained in a gangue of limestone or dolomite. Or, the ore might carry nickel and copper with a sulfide assemblage of pentlandite $(Fe, Ni)_9S_8$, chalcopyrite, and pyrrhotite in a gangue of altered quartz diorite. In such ores the minor associates may be increased by those normally accompanying lead and zinc, for example, by cadmium and antimony.

Copper itself may occur as a by-product in some ores, and its value may be only a subordinate item in such deposits.

Copper ores vary widely in tenor, but usual practice is to group them into "high grade" and "low grade" categories. In the United States at present most copper comes from the mining and concentrating of ores carrying from 0.40 to 1.20 per cent copper in the sulfide form, and the general average content of recoverable copper is about 0.85 per cent. High-grade ores commonly contain from 3 to 10 per cent copper, although some may be richer, and are generally smelted direct without preliminary concentration.

Among the sulfide copper ores, three outstanding groups should be noted. The first is composed of the "porphyry copper" and Northern Rhodesian types which carry copper mostly in the form of chalcocite, chalcopyrite, and bornite with iron being contained in pyrite, chalcopyrite, and bornite. Copper ranges in amount from a fraction of one per cent to several per cent, and iron is generally low to moderate in amount. A second group includes the deposits commonly known as "cupriferous pyrite" bodies. These contain very abundant pyrite and pyrrhotite and thus are high in iron and sulfur. Copper is carried in these ores by chalcopyrite, or occasionally by chalcocite and covellite, and is generally low to moderate in amount. Notable examples are at Jerome, Arizona; Rio Tinto, Spain; and Cyprus. A third group comprises the ores carrying copper in the form of enargite or tennantite, which contain arsenic. Well-known deposits of this kind are at Butte, Montana; Bor, Yugoslavia; the Cordilleran region of South America; and Tsumeb, South West Africa.

Various groupings of oxidized copper ores may be made according to their response to metallurgical treatment. Thus, for example, we may recognize (1) the malachite-bearing ores in dolomite of the Belgian Congo, which are successfully concentrated by flotation; (2) the various mixtures of malachite, azurite, chrysocolla, and tenorite that are subject to treatment by leaching with sulfuric acid; and (3) the unusual oxidized mineral assemblage at Chuquicamata, Chile, consisting principally of brochantite, atacamite, antlerite, chalcanthite, krohnkite, and natrochalcite, also treated by leaching.

In addition, there are various mixtures of oxidized and sulfide copper minerals occurring together in ores that are treated by leaching.

Besides the various types of copper ore noted above, there are those in which copper is carried as the native metal. In these the gangue may be conglomerate or basalt, as in the ores from Michigan, or sandstone, as in the much smaller deposits at Corocoro, Bolivia.

The kind of gangue accompanying a copper ore may be of considerable importance in its mining and treatment. The mineralogy, texture, and physical characteristics of the gangue, which is generally the preponderant material, may dictate the type of mining method to be employed. Similar factors control crushing, grinding, classification, and flotation of the ore during its treatment.

Copper ores are found with diverse textures, depending upon the size, relative abundance, and arrangement of their constituents. Ores in which the sulfide grains are scattered through the host rock as seed-like particles are properly termed "disseminated ores." On the other hand, where the sulfide minerals are aggregated together in rich abundance, the ore is designated as "massive sulfide." Or, if the valuable minerals occur in a multitude of little veinlets, it is called a "stringer ore," or perhaps a "stockwork."

The mineral composition and relative abundance of valuable constituents and gangue determine the chemical composition of an ore. Table 2-2 lists various typical examples, inspection of which will show the great variation among representative individual ores. The types of ore and their localities, corresponding to the numbers heading the columns in the table, are given on page 27, together with the sources of the data.

TABLE 2-2. CHEMICAL ANALYSES OF VARIOUS COPPER ORES

	1	2	3	4	5	6	7	8	9	10	11	12
SiO_2	65.57	71.28	65.5	54.79	64.17	47.72	37.20	22.90	40.10	23.10	11.80	0.71
Al_2O_3	15.42	13.53	13.6	17.97	7.42	7.89	3.70	12.70	12.50		3.50	0.53
Fe_2O_3	1.05	0.61										
FeO	2.40	1.00				20.00						
MgO	1.66	0.41		4.78	5.05	16.08						0.60
CaO	0.39	0.17	2.6	1.30	1.29	2.84	0.64	1.22	1.05		1.80	0.19
Na_2O	3.33	0.31										
K_2O	5.01	3.81										
H_2O-	0.79	0.31										
H_2O+	1.06	1.90										
TiO_2	0.36	0.47										
P_2O_5	0.23	0.09										
MnO	0.03	Nil										
Cu	0.82	1.00	0.88	3.24	9.31	2.61	5.44	4.73	2.79	3.40	4.99	10.02
FeS_2	0.20	4.86										
Fe			2.2	3.22	3.21		21.40	20.70	15.70	33.25	31.40	39.47
S			1.1	0.95		0.87	21.30	15.40	10.80	19.80	32.60	48.39
Ni										3.00		

1. Porphyry copper ore (monzonite), Ajo, Arizona. From Gilluly, J., *U. S. Geol. Surv. Prof. Paper* 209 (1946).
2. Porphyry copper ore (schist), Ray, Arizona. Ransome, F. L., *U. S. Geol. Surv. Prof. Paper* 115 (1919).
3. San Manuel porphyry ore. Chapman, T. L., *U. S. Bur. Mines Repts. Investigations* No. 4108 (1947).
4. Roan Antelope, ore in shale, Northern Rhodesia. Newton, J., and Wilson, C. L., "Metallurgy of Copper," John Wiley & Sons, Inc., New York, 1942.
5. Katanga, high-grade malachite leaching ore, Belgian Congo. Newton, J., and Wilson, C. L., *idem.*
6. Namaqualand copper ore in norite, Nababeep South mine, Cape Province, Union of South Africa. Banghart, M. D., and Pennebaker, E. N., *Eng. Mining J.*, 148, 79 (Jan., 1947).
7. Siliceous copper ore, United Verde mine, Jerome, Arizona. Reber, L. E., Jr., *Univ. Ariz. Bull.*, 145 (1938).
8. Schist copper ore, United Verde mine, Jerome, Arizona. Reber, L. E., Jr., *idem.*
9. Quartz porphyry copper ore, United Verde mine, Jerome, Arizona. Reber, L. E., Jr., *idem.*
10. Copper-nickel ore, Sudbury, Ontario. Newton, J., and Wilson, C. L., *idem.*
11. Massive sulfide ore, United Verde mine, Jerome, Arizona. Reber, L. E., Jr., *idem.*
12. Massive pyritic ore, Ergani mine, Turkey. Birgi, S. E., *Eng. Mining J.*, 151, 92 (April, 1950).

In summary, the type of copper ore (whether oxidized or sulfide), its richness in copper, the amount of accompanying metals of value, the content of substances detrimental to treatment, the kind of gangue, and the texture and hardness of the ore all influence the selection of methods for its treatment. Of the copper derived from copper ores in the United States, about 94 per cent is obtained from ores concentrated before smelting, approximately 2 per cent comes from direct smelting ores, and 4 per cent is from ores treated by leaching.

Copper Ore Deposits

Classification

Ore deposits containing copper may be subdivided into various groups based on several systems of classification. For example, they may be classified according to form, whereby veins, stockworks, blankets, pipes, and lenses of ore are recognized. Or, copper ore bodies may be grouped according to the kind of rock enclosing the deposit or in which the valuable mineral is found. Thus, there are copper deposits associated with norite, or diorite, or monzonite; there are the so-called "limestone deposits" with copper ore bodies variously disposed in that kind of rock; and there are copper deposits in sandstones which display a scattering of copper-bearing minerals throughout certain sedimentary layers.

Again, copper deposits may be classified according to the type of copper mineral present, or according to an accessory metal associated in important amounts. Or, the occurrence may be classified with respect to its geologic age.

When making reference to various copper ore deposits or districts, it is common practice to designate a particular individual one on a basis of classification that brings forward certain well-known features. Thus, we may speak of the "porphyry copper" deposits, or the "cupriferous pyrite" deposits, or the "sedimentary copper" deposits.

However, the geologist generally prefers to classify copper and other ore bodies according to their mode of origin. Such a genetic classification recognizes a number of different processes by which copper ore bodies may have been formed. A simplified arrangement of these is as follows:

(A) *Syngenetic,* or contemporaneous in age of formation with the enclosing rock:
  (1) Magmatic segregations (hypogene).
  (2) Sedimentary deposits.
(B) *Epigenetic,* or younger in age than the enclosing rock:
  (1) *Hypogene:* due to solutions or gaseous emanations rising upward from magmatic sources:
    (a) Contact-metasomatic deposits.
    (b) Hydrothermal deposits.
      Cavity fillings or replacements.
  (2) *Supergene:* modifications caused by rearrangement of metals due to processes of weathering, ground-water movement, and precipitation.

Modes of Origin

Ore deposits originate by *magmatic concentration* where minor constituents of igneous magmas have become concentrated to form bodies of adequate size and richness. Such deposits result from simple crystallization, or from concentration by differentiation, of igneous masses. There are several modes of formation of magmatic deposits, and they may originate during different periods of magma crystallization. American investigators now believe that very few important copper deposits have been formed by magmatic segregation, although such an origin is maintained for a number of deposits by others who have studied them.

The process of *sedimentation* has formed not only sedimentary rocks (such as shale, sandstone, and limestone) but it has also given rise to valuable mineral deposits. Their mode of origin is that of sedimentation with special conditions to account for the bringing together of valuable metals. A syngenetic sedimentary origin is advocated in the case of a few copper deposits, but, as Bateman advises, not without dispute. The "Red Bed" copper deposits of the southwestern United States are believed to be of sedimentary origin with subsequent rearrangement by other processes. The Central African copper deposits of Northern Rhodesia are considered by some to have originated by sedimentary processes, although a hydrothermal origin is vigorously maintained by others.

Ore deposits formed by *contact metasomatism* are those located near the margins of igneous bodies and believed formed by escaping gaseous emanations of high temperature during or shortly after the consolidation of intrusive magmas. Thus an accession of valuable metal from the magma is involved, along with recrystallization and recombination of material composing the invaded rock. Such deposits are generally irregular in shape and are of comparatively small size. Certain copper deposits, mostly in impure limestone, are believed to have originated by this process. Besides containing chalcopyrite, bornite, pyrite, and pyrrhotite, the gangue is distinctive and commonly carries magnetite, quartz, carbonates, and a considerable variety of silicates, including various kinds of garnet.

Most of the world's important copper deposits are believed by many to owe their origin to *hydrothermal processes.* This theory holds that water solutions derive metals from a consolidating intrusive body of igneous rock that is undergoing magmatic differentiation and that such solutions transport these metals upward and outward to sites of ore deposition. The solutions are, or become, liquids and they lose heat with added distance from the intrusive center, with the result that they give rise to high-temperature hydrothermal deposits near the intrusive and lower temperature deposits farther outward. During their journey through bedrock, hydrothermal solutions may deposit their mineral content in various kinds of openings to form cavity fillings, or deposition may take place by metasomatic replacement away from cavities thus giving rise to replacement deposits, or there may be a combination of both types of deposition. For the process to operate, rock openings are necessary to transmit enormous volumes of mineral matter in solution to sites of deposition. Mineral deposits so formed are generally accompanied by zones of altered wall rocks due to mineral changes effected by the hydrothermal solutions. The localization of the deposit is controlled by a number of features, and the consideration of this subject is one of the important branches of economic geology.

Ore deposits formed by magmatic segregation, contact metasomatism, and hydrothermal solutions are termed "hypogene," implying formation by ascending solutions, and in this sense the term "primary" is generally considered synonymous. On the other hand, changes brought about by weathering and oxidation as a consequence of descending surface waters are called "supergene," and for this the word "secondary" is commonly used synonymously.

Secondary, or supergene, changes wrought in copper deposits by erosion and consequent weathering may be of great importance. By such action, hypogene copper sulfides may be converted into copper oxides at and near the earth's surface, and these oxides may extend downward from several tens to several hundreds of feet. On the other hand, copper may be cleanly leached from surficial rocks and carried downward by surface waters to near ground-water level where it may be precipitated under reducing conditions upon, and thus replace and enrich, sulfides formed earlier. Numerous deposits have had their tenor in copper raised by such supergene, or secondary, enrichment by an amount sufficient to permit them to be exploited as ores.

Production Data

World production of copper from ore bodies in 1952 is estimated at approximately 2,986,000 tons of metal. Copper supplied from ore deposits by the six leading countries was as follows for 1952:

	Short Tons of Metal	Per Cent of World Production
United States	932,600	31.2
Chile	446,100	14.9
Northern Rhodesia	327,200	11.0
Russia	325,000	10.9
Canada	258,900	8.7
Belgian Congo	226,800	7.6
		84.3

As regards production of copper in 1952 from various classifications of ore deposits, the following approximation will serve to illustrate the importance of certain types:

	Short Tons of Metal	Per Cent of World Production
Porphyry copper deposits	1,220,000	40.9
Central African copper belt	554,000	18.6
Sudbury basin	125,500	4.2
Butte, Montana	57,800	1.9
		65.6

The remaining world production, approximately one-third of the total, comes from a variety of copper ore deposits in addition to the types listed above.

EXAMPLES OF COPPER ORE DEPOSITS

The following deposits are selected to describe the various sources contributing to present production, and a few examples of ore bodies that were formerly outstanding but are now mined out are also included.

Two principles have been followed: (1) examples have been chosen to show the variety of conditions under which copper ore is found, with accent on those that are now the most important sources of supply, and (2) descriptions have been extended to give a brief survey of deposits outside of the Americas. Thus the most important geologic types contributing to present-day output, the porphyry coppers and the Central African deposits, are described first; these are followed by an account of several deposits from classical localities; and then the foregoing are followed by a survey of remaining fields along geographical lines.

The important copper-producing regions of the world are (1) the western and southwestern United States, where numerous great deposits of copper and other metals are erratically clustered outside the arcuate front of the Colorado Plateau; (2) the western slope of the Andes in Peru and Chile; (3) the central African province in Northern Rhodesia and the Belgian Congo; (4) the Precambrian area of central Canada; (5) the Keweenaw Peninsula of northern Michigan; and (6) various localized rich centers of relatively limited size in many parts of the world.

For illustrations of the geological relations of many of the ore deposits described in the following pages, the reader's attention is directed to the selected references listed at the end of this chapter.

Porphyry Copper Deposits

The porphyry copper deposits comprise a group of nine producing districts in the southwestern and western United States, one district in Mexico, a small deposit in Canada, three districts in South America, and possibly several districts in Asiatic Russia. In addition, in the southwestern and western United States there are five other districts with porphyry copper ore bodies in various stages of exploration and development, and there are also four of this type currently known in South America.

The terms "porphyry copper" deposits and "disseminated copper" deposits are applied in the mining industry to this group of very large, low-grade ore bodies that are presently the backbone of the world's copper production, and these designations have been carried over into both geologic literature and popular usage. The typical porphyry copper deposit is generally large in horizontal extent as compared with vertical depth; it consists of ore of low tenor, and is amenable to mass production methods of extraction and treatment. Individual ore bodies range in size from several tens of millions of tons up to a billion tons. The contained copper minerals are usually few in number, simple in composition, and rather evenly distributed throughout the ore.

The designation "porphyry copper" is derived from the fact that many (although not all) of such deposits display copper minerals deposited in host rocks classified as quartz monzonite porphyry or in related rock types. However, not all of the so-called porphyry coppers are found in monzonitic igneous rocks, and it is noteworthy that large tonnages at Miami, Inspiration, and Ray, all in Arizona, are in schist with monzonitic rocks nearby and that volcanic rocks carry a similar type of ore at Cananea and at Rancagua, Chile.

In many porphyry copper deposits from 50 to 90 per cent of the copper, in the form of sulfide grains, is distributed along thin fractures that make up a complex pattern of small-scale rock breaking. The remaining portion of the sulfide grains is scattered through the host rock in "disseminated" fashion resembling seed-like particles. Some of these disseminations are more apparent than real because many grains have been deposited in fractures earlier healed by quartz and sericite.

Porphyry copper deposits may be subdivided into four groups according to the type of copper minerals contained:

(1) Deposits with copper in the form of secondary sulfides.
(2) Deposits with copper in the form of primary sulfides.
(3) Deposits containing mostly oxidized copper minerals.
(4) Deposits of mixed oxides and sulfides.

(1) Many porphyry copper deposits were formed by the secondary enrichment of lean primary sulfides. As previously described, primary material carrying, for example, chalcopyrite and pyrite to give a copper content of around, say, 0.25 per cent, was leached by surface waters and the copper precipitated at depth in the form of secondary, or supergene, chalcocite to build up, by continuing repetition of the process, an ore of commercial tenor. Because of their relation to earth's surface and ground-water level, these enriched deposits generally have the form of undulating blankets with relatively large horizontal dimensions and a depth range usually limited to a few hundred feet. Besides secondary chalcocite, covellite may also occur as an associated copper mineral of secondary origin. In addition, unreplaced pyrite and chalcopyrite are commonly present and other sulfides may be found in minor amounts. Secondary ores are readily amenable to concentration by flotation.

(2) In some districts the tenor of primary mineralization itself is sufficient to constitute an ore of copper, and, where it remains buried at such depth that it has escaped weathering and secondary enrichment, there may be a "blind" ore body of the porphyry copper type free from oxidation or enrichment. Or, another variety of primary deposit may occur below where copper is oxidized and fixed in the capping without migration downward to effect enrichment. In this case, given a primary

tenor of sufficient richness, there may be a commercial primary deposit (say, with copper in the form of chalcopyrite) overlain by a zone of oxidized copper minerals with copper content of about the same tenor as that of the primary zone. Or, another arrangement may be found where the overlying blanket of enriched sulfides averages in grade, say, from 1.5 to 2.0 per cent copper, with the underlying primary zone at 0.6 to 1.0 per cent copper. In the earlier days of porphyry copper exploitation only the enriched blanket was treated as ore; however, due to improved techniques developed in mining and beneficiation, the underlying primary zone was eventually considered ore and was extracted. Primary deposits are not confined to a blanket-like form, but may escape downward in the shape of pods, plugs, wedges, or prongs. The dominant copper minerals are commonly chalcopyrite, bornite, enargite, and primary chalcocite with pyrite as an associate. Molybdenite may be present (both in primary and secondary deposits) and in some districts is *recovered for the production of molybdenum. Primary porphyry copper* ores are particularly amenable to concentration by flotation.

(3) Where primary mineralization is relatively low in sulfur, or where gangue minerals are particularly reactive, copper may be oxidized and fixed in the outcrop and the near-surface zone, as previously pointed out. Thus, there may be formed relatively shallow bodies of oxidized porphyry copper ore—either as fairly regular blankets overlying primary ore bodies, or as blankets or erratic lenses with secondarily enriched ore below, or in various other arrangements. Oxidized ores of low tenor require special methods of treatment, the copper usually being recovered by leaching and precipitation.

(4) In the above arrangement, the distribution of oxidized and sulfide ores may be such that they must be mined as a "mixed ore."

Associated with mineralization of the porphyry copper type are various chemical changes imposed upon the host rocks. Generally they have been severely altered and converted to sericite, clay minerals, and chlorite with variable silicification. Thus the gangue, which constitutes the bulk of the ore, is "remade," and it is this material that is mostly eliminated by concentration of the ore during the treatment process.

Brief Descriptions of Porphyry Copper Deposits

Bingham, Utah. Illustrative of the great productive capacity of certain porphyry copper deposits, the ore body at Bingham supplied 31 million tons of ore during 1950. The deposit has the form of a huge oval drum with (1) limited amounts of oxidized ore in the superficial portion followed at depth by (2) enriched sulfides, and (3) mixed enriched and primary sulfides, the enriched sulfides decreasing with added depth. The ore body is 6,000 feet long by 4,000 feet wide and at least 2,500 feet deep, its shape being unknown at depth. The mining grade is about 0.9 per cent copper; molybdenite is recovered from the concentrates. This ore body supports one of the largest open-cut operations in the world.

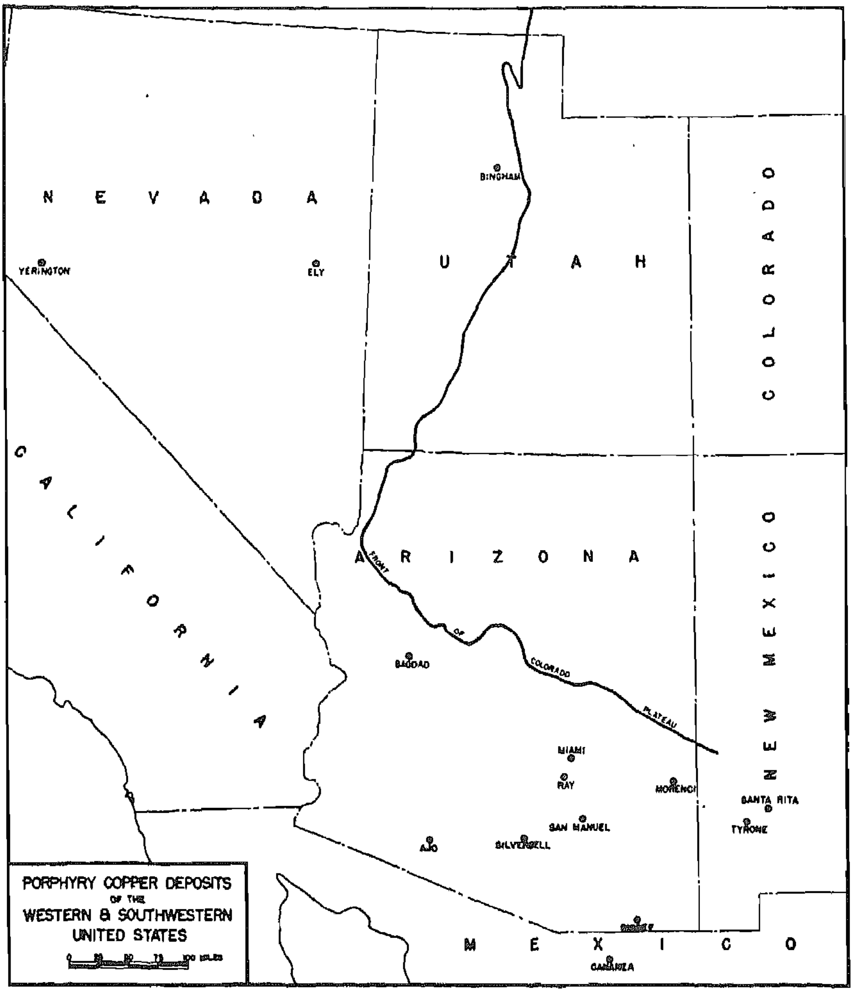

Figure 2-1.

Ely, Nevada. The Ely ore-bearing zone is dominated by a number of older monzonite porphyry intrusions in remarkable east-west alignment for six miles. Several of these bodies, along with some of the adjacent limestone, are metallized to form porphyry copper deposits. The upper parts of certain ore bodies were importantly enriched, but the bulk of the ore owes its value in copper to primary chalcopyrite. The Emma Nevada deposit on the west is essentially a buried primary ore. The district has been a major producer of copper, gold, and silver for 25 years, with important open-pit and underground mining operations.

Santa Rita, New Mexico. The Chino ore body at Santa Rita occurs in a rounded body of granodiorite porphyry about a mile across. Veins and disseminated grains of chalcocite are found abundantly in altered porphyry along with pyrite. Some believe that chalcocite may belong to a late phase of hypogene mineralization as well as being developed by supergene enrichment. Parts of the ore body consist of oxidized ores carrying native copper, cuprite, and malachite. The Chino deposit is the site of large open-pit operations.

Ray, Arizona. At Ray an extended blanket-like deposit has been developed in the Pinal schist by multiple enrichment of lean primary material. Long the scene of large-scale underground mining, open-cut operations are now established above and outward from the old workings.

Ajo, Arizona. The great ore body at Ajo is roughly elliptical in plan and is 3,600 feet by 2,500 feet across. Most of the ore occurs as a rather flat lens with a deeper keel, although at the south end a tongue plunges steeply southward to great depth. The bulk of the ore is in quartz monzonite with some in bordering volcanic rocks. The ore body was oxidized to a level plane, above which copper is in the form of malachite with minor azurite, cuprite, tenorite, and chrysocolla. Below this is primary sulfide ore with chalcopyrite, some bornite, and a little pyrite. Minor tennantite, sphalerite, and molybdenite are also present. The tenor of the ore body was essentially the same in both the oxidized and sulfide zones, and this, in conjunction with trivial secondary enrichment, points to little migration of copper during weathering. The upper blanket of oxidized ore was treated by sulfuric acid leaching. The ore body supports a great open-pit operation.

Miami, Arizona. Near Miami, Arizona, the Miami-Inspiration ore zone follows a broad arc northeasterly for 12,000 feet near but just outside of a lobe of granite porphyry. An extended deposit of ore, mostly in Pinal schist, has been developed in the form of an inclined blanket that abuts the Miami fault on the east. The ore bodies have been formed by secondary chalcocite enrichment that has approximately tripled the copper content of the primary material. The top of the sulfide zone of the Miami ore body is beneath 300 to 450 feet of leached capping; the ore body varies in thickness from 325 to 750 feet. The ore zone is the site of extensive underground mining. On the west, where oxidized copper minerals are fixed in the capping, an open-cut operation has been established.

Also near Miami occur the smaller Castle Dome and Copper Cities low-grade deposits in quartz monzonite and quartz monzonite porphyry. The former has been mined out by open-cut methods, whereas mining operations are just now being established on the latter. These ore bodies carry chalcocite, covellite, chalcopyrite, and pyrite with lesser amounts of a few other sulfides, including molybdenite. Supergene enrichment has about doubled the primary tenor.

Morenci, Arizona. The Clay ore body at Morenci supports one of the great open-pit operations of Arizona. Multiple enrichment of lean primary material has formed an immense body with secondary chalcocite and pyrite in diorite porphyry.

Bagdad, Arizona. The ore body at Bagdad is a typical chalcocite blanket formed by enrichment of hypogene sulfides. The richer ore consists of secondary chalcocite which replaces chalcopyrite in preference to pyrite, but lean primary ore occurs at depth. A noteworthy amount of molybdenite is present. Mining operations have been changed from underground caving to open cut.

Tiger, Arizona. The San Manuel ore body near Tiger, Arizona, is the newest American discovery of great size and is now in process of being developed by underground methods. The copper minerals are disseminated throughout an extensive zone in quartz monzonite and monzonite porphyry. Sulfide enrichment is variable, with the increase in copper tenor averaging only a few tenths of one per cent. Chalcopyrite, chalcocite, and pyrite are the most abundant sulfides, with bornite and covellite also being present. Reserves are near one-half billion tons that average 0.78 per cent copper. Of this, 123 million tons is oxidized and averages 0.77 per cent copper, most of which is carried by chrysocolla and possibly cuprite.

Silver Bell, Arizona. At Silver Bell, about 40 miles northwest of Tucson, a body of porphyry copper ore occurs in a complex of intrusive igneous rocks and has recently been prepared for exploitation by open-cut mining. In this deposit secondary chalcocite replaces pyrite and chalcocite and thereby enriches the primary metallization to the extent that it can be mined as an ore.

Yerington, Nevada. A deposit of porphyry copper ore has recently been brought into production at Yerington. The upper part of the ore body is oxidized with the development of copper oxides and carbonates, and ore from this section is mined by open-cut methods and then copper is extracted by leaching with sulfuric acid in vats.

Tyrone, New Mexico. At Tyrone, a long-known deposit of disseminated chalcocite and pyrite in quartz monzonite porphyry is being extended laterally by churn drilling.

Bisbee, Arizona. At Bisbee, porphyry copper ore in the central granitic stock of Sacramento Hill and adjacent mineralization is being prepared for extraction by large-scale open-cut mining.

Cananea, Sonora, Mexico. A large, low-grade body of porphyry ore was brought into production at Cananea in 1944.

Copper Mountain, British Columbia. At Copper Mountain a volcanic breccia of andesite fragments is mineralized by bornite and chalcopyrite adjacent to a gabbro stock. The deposit is thus a variety of porphyry copper with primary ore.

Chuquicamata, Chile. The great porphyry copper deposit of Chuquicamata is in northern Chile in the Atacama Desert, one of the world's most arid regions. This extreme aridity has permitted the development of large quantities of sulfate and other water-soluble minerals that normally would be carried away by rainfall and has thus given rise to a huge, overlying deposit of oxide ore with a great diversity of copper-bearing minerals. The ore body is roughly pear-shaped with a length of 2 miles by 3,600 feet maximum width and over 1,500 feet deep and is in the midst of a large body made up of granodiorite and monzonite porphyry. Mineralization is related to extensive fracturing and shearing accompanied by heavy silicification and sericitization. Primary sulfides are pyrite, enargite, chalcopyrite, possibly primary chalcocite, and scattered molybdenite; these have been replaced and enriched to considerable depth by secondary chalcocite, and chalcopyrite has to some extent been replaced by covellite. Weathering has produced (1) an upper zone of oxide ore underlain by (2) a zone of iron oxide waste, (3) a succeeding erratic zone of mixed oxide and enriched sulfide ore, and (4) an underlying zone of enriched sulfide ore. In the past, mining operations were confined to the oxide ores, but construction is now about completed on a new plant for treatment of sulfides. The oxide ores contain a number of unusual copper minerals which are formed in the Atacama Desert. These include, among others:

Antlerite	$Cu_3(SO_4)(OH)_4$
Atacamite	$Cu_2Cl(OH)_3$
Chalcanthite	$CuSO_4.5H_2O$
Krohnkite	$Na_2Cu(SO_4)_2.2H_2O$
Brochantite	$Cu_4(SO_4)(OH)_6$
Natrochalcite	$Na_2Cu_4(SO_4)_4(OH)_2.2H_2O$

As Bateman points out, "The primary mineralization attended the porphyry intrusion. Oxidation and leaching during the damp middle Tertiary climate produced a leached capping and a deep supergene sulfide zone. The Pliocene uplift initiated erosion, removed most of the capping, and during the arid climate converted the upper part of the sulfide zone to the oxide ores." Thus the largest of the presently known porphyry copper deposits was formed.

Potrerillos, Chile. The three ore bodies of Potrerillos are similar to those of Chuquicamata, although smaller in size, and are typical stockworks. The host rock, a quartz diorite porphyry, has been intensely altered along with the deposition of pyrite, chalcopyrite, and enargite plus minor tetrahedrite, sphalerite, galena, and molybdenite, and the sulfide ore has been enriched by chalcocite and covellite. Oxide ore occurs in important amount, the chief copper-bearing minerals being brochantite and antlerite with some copper oxides, carbonates, and silicates. Beneath the oxide ore is another leached zone, which is succeeded in turn by the zone of enriched sulfides.

Rancagua, Chile. The Braden copper deposit at Rancagua is found about the periphery of what some investigators believe to be an old volcanic vent that pierces a mass of igneous rocks. Here economic mineralization occurs principally as quartz, pyrite, and chalcopyrite in irregular fractures that cut through andesite porphyry. Secondary enrichment has improved the tenor of the upper part of the ore body by addition of chalcocite and covellite. Besides copper, molybdenite is also commercially extracted.

Peru. In Peru, exploration has revealed porphyry copper deposits at Toquepala and Quellaveco, and other bodies are known to occur elsewhere.

Central African Copper Province

The Central African copper province extends northwesterly through Northern Rhodesia for 140 miles along the Belgian Congo border to near Kipushi, where it crosses into the Congo and continues for an additional 180 miles. The spectacular development of the Northern Rhodesian copper belt since 1927 has placed it third among the world's copper producers. The Katanga district of the Belgian Congo was earlier known and has been a substantial supplier of copper since 1911; in 1952 it stood in sixth place.

Ore reserves currently reported for Northern Rhodesian mines amount to nearly 700 million tons varying in grade from 2.5 to 7.0 per cent copper. Katanga reserves are reported to be about 10 million tons of copper in ore averaging about 6 per cent. It is to be expected that substantial additions will be discovered as exploration continues in these prolific fields.

Northern Rhodesia Ore Deposits. The copper ores of Northern Rhodesia occur in sedimentary beds underlain by metamorphic and igneous rocks and overlain by a thick series of younger sediments. The sedimentary rocks have been strongly folded into a series of complex anticlines and synclines. Erosion has planed away the anticlines leaving the synclines preserved as down-folded basins in the older underlying rocks. It is within portions of these synclinal remnants that copper deposits are found in what is known as the Lower Roan group of sandstones and conglomerates, which also contains associated thin beds of shale and dolomite.

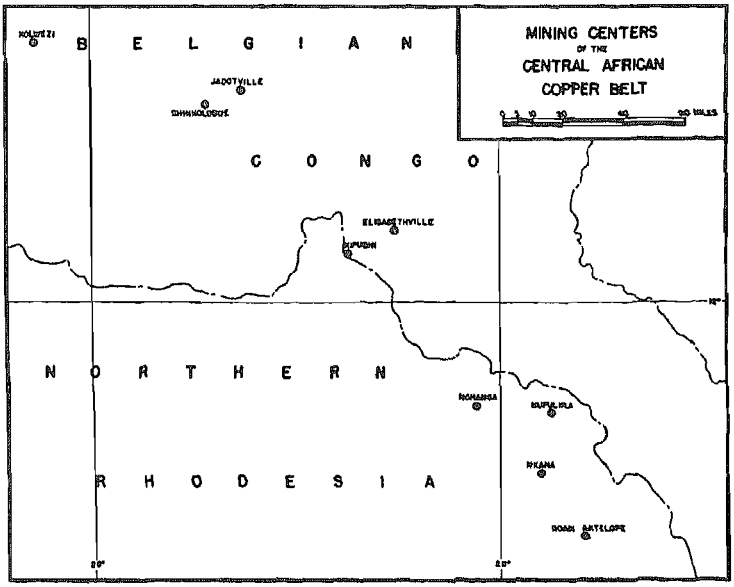

FIGURE 2-2.

In the Rhodesian field a number of commercial ore deposits have been developed. These include Roan Antelope, Mufulira, Chambishi, Baluba, Nkana, Nchanga, Nchanga Extension, and Chingola. More recently, additional ore bodies have been developed at Konkola, Kirila Bomwe North, and Kirila Bomwe South. The valuable copper mineralization occurs in a shale, argillite, graywacke, or quartzite horizon found near the base of the Lower Roan group, the exact horizon depending on where the copper deposit is situated. The ore bodies are generally very extensive and remarkably even in copper content and width. They represent large-scale disseminated deposits, and, being confined to certain sedimentary beds, their outlines are similar to the parts of the synclinal folds that are metallized.

The Northern Rhodesian deposits consist of one or more beds in which fine grains of copper sulfides have been abundantly deposited. The copper-bearing minerals are chalcocite, bornite, and chalcopyrite with very minor amounts of other metallic minerals. The ore deposits are low in iron, and pyrite is an uncommon mineral. The gangue is composed principally of the host rock. Most of the ore bodies consist of sulfide ore, but in places they may be oxidized to variable degree, and considerable oxidized ore is mined in certain sections. Cobalt is an important by-product of the Nkana mine, making Northern Rhodesia the world's third-largest producer of that metal.

Both primary and secondary chalcocite are present in Rhodesian ores, but the amount of secondary enrichment is debatable. In general, chalcopyrite and bornite become more abundant at depth, whereas chalcocite is less so. Regardless of the amount of sulfide enrichment, the commercial tenor of the ore is not dependent upon enrichment, and the ores persist at depth. The deposits are characterized by rather even metallization, and the copper-bearing beds are cleanly separated from the adjacent strata that bound them.

At the *Roan Antelope* mine the productive bed has been folded to give an asymmetric syncline that plunges northwestward. The Roan Antelope deposit is important for the great length of ore developed around the nose and along the limbs of the fold, possibly aggregating 9 miles in length with an ore bed thickness of from 25 to 30 feet.

The *Baluba* deposit lies on an extension of the north limb of the Roan syncline. It is more limited in size and exhibits complicated minor folding.

The *Mufulira* mine is found on the southwest limb of a major syncline. The structure is relatively simple with the flank of the fold dipping at 45 degrees. There are three parallel mineralized beds at Mufulira separated by 25 to 45 feet of waste. The two lower beds coalesce toward the northwest to give a thickness of over 100 feet in places.

A closed syncline near the center of the copper belt contains the *Chambishi* and *Nkana* ore bodies. The Chambishi is exceptionally complicated with overturned, closed, and faulted folds that involve an ore bed that averages 25 feet thick. In the Nkana sector, two ore bodies, the Nkana and Mindola, are recognized. The Mindola ore follows the simple steep limb of the fold, whereas the Nkana is complicated by folds plunging flatly northwest. The average thickness of the ore bed is about 30 feet.

The *Nchanga* mine is found toward the northwest in another synclinal structure, which also carries the Nchanga Extension and Chingola deposits. Ore is found at different stratigraphic horizons on the two limbs of the structure. Partial oxidation of the ore persists to the greatest depth explored.

In summary, the Northern Rhodesian copper deposits are found in a number of synclinal structures preserved along a belt 140 miles long and about 40 miles wide. They occur as disseminations in certain stratigraphic horizons, the latter varying somewhat in position and character from place to place. The copper-bearing beds range in thickness from a few tens of feet up to 100 feet; they extend on strike for a few thousand feet to a few miles and persist at depth for a known distance of several thousand feet.

The origin of these deposits is a subject of debate. Their extended distribution in thin sedimentary beds has led to the view that the copper was deposited by sedimentary processes at the time the beds were laid down. On the other hand, various investigators point to compelling evidence favoring hydrothermal origin by solutions that were a phase of igneous activity.

Belgian Congo Ore Deposits. From Northern Rhodesia, the Central African copper province extends well into the Belgian Congo to where it ends against basement rocks. Along its course, copper deposits are found in three clusters: (1) a southeastern group in the environs of Elisabethville, (2) a central group near the industrial center of Jadotville, and (3) a western group near Kolwezi.

Geological relations in the Belgian Congo field are similar to those of Northern Rhodesia except for tighter folding and more abundant faulting. Yet copper deposits in the Congo are found in the Upper Roan group of dolomite and dolomitic shale, whereas in Rhodesia they appear in the Lower Roan group of sediments.

Most of the better-known copper occurrences consist of oxidized ore and are generally found at or near the surface. Ore deposits range in size from small bodies to those large enough to support open pits worked by power shovels. The common oxide minerals are malachite and chrysocolla with lesser amounts of cuprite and native copper. The copper found in the oxidized minerals has been transported to its present site, presumably from other deposits in higher horizons now eroded away. Some of the copper ore bodies carry appreciable amounts of cobalt in the form of black oxide, and cobalt is recovered as a by-product to such an extent that the Belgian Congo is at present the largest producer of this metal.

Although mines with oxidized ores are still the more important source of copper in the Congo, certain deposits at depth occur as bedded sulfides carrying copper and cobalt with a little gold and metals of the platinum group. The copper sulfides at Fungurume are found in two dolomitic horizons and consist of bornite, chalcocite, and covellite. Substantial tonnages of the ores range in tenor from 5 to 8 per cent copper with accompanying cobalt in amounts not exceeding 0.4 per cent. The sulfides appear as disseminated grains with a maximum size of 0.5 millimeter. At Kambove-West, deep sulfide copper deposits will soon be exploited. Thus there are indications of a new phase in mining developments of Katanga, which are turning toward the exploitation of deep primary sulfide deposits of large tonnage.

In addition to the bedded deposits mentioned above, the Prince Leopold mine at Kipushi is a pipe-like replacement of sulfides in calcareous breccia and schist, giving a mineralized zone 2,400 feet long. Its ore consists of bornite, chalcopyrite, and sphalerite with subordinate galena from which copper, zinc, and lead are recovered.

The famous Shinkolobwe uranium deposit is found as a member of the central cluster of ore occurrences near Jadotville. Besides uranium it contains copper, cobalt, and nickel.

Other Copper Deposits of the United States

Butte, Montana. The copper deposits of the Butte district are superb examples of copper mineralization in the form of a great complex of veins. From an area only 2.5 miles wide, 5 miles long, and about three-fourths of a mile deep, approximately 6.75 million tons of copper metal have been won. In addition, considerable amounts of silver, gold, zinc, and lead, along with some manganese have also been produced.

The host rock is locally called the "Butte granite" and is a portion of the granodiorite Boulder batholith near its western border. Barren aplite and quartz porphyry dikes intrude the host rock and are in turn cut by seven systems of faults.

The copper deposits occur as steeply inclined veins deposited in three of these fault systems. They vary in width from a few feet to a few tens of feet and may persist as far as 7,000 feet in length. Each later fault system cuts and offsets the earlier, and the result, as aptly described by Bateman, is a complex parquetry of vein or fault segments.

The oldest fissures, termed the Anaconda, trend easterly and dip steeply south. They are long and wide, and persist at depth. These veins are rich and rather continuously mineralized, and they have been the great producers at Butte. The Blue system strikes northwest and dips steeply southwest, and its members cut the Anaconda system. Their ore is characteristically discontinuous and confined to irregular bodies. The Steward system strikes northeast, and its veins dip steeply southeast. These displace veins of the two older systems and carry ores in minor amounts.

East of the point where the Anaconda vein of the Anaconda system becomes discontinuous, mineralization is represented by a series of segments arranged *en echelon.* Ore in this area occurs in numerous veinlets striking northwest with a stockwork of connecting stringers, irregular lenses, and disseminations of copper-bearing sulfides. This intensely fractured "horsetail" area is about 2,000 feet long, from 300 to 500 feet wide, and extends down below the 3,400-foot level. It is now planned to mine much of this zone as a low-grade ore body by large-scale methods.

The three vein systems and the "horsetail" zone contain identical ores that apparently were all formed during the same period of mineralization. The four later systems are post-mineral faults that cut and displace the ore-bearing veins, giving rise to disconnected segments of the latter.

The principal copper minerals of the Butte ores are chalcocite, enargite, bornite, chalcopyrite, tennantite, tetrahedrite, and covellite. The gangue minerals are mostly quartz and pyrite. The zinc sulfide, sphalerite, is abundant in certain zones, as is also the manganese carbonate, rhodochrosite.

The oxidized section is about 300 feet deep, below which is a shallow zone of secondary enrichment carrying "sooty" chalcocite. Below this the chalcocite is the steely variety deposited by hypogene solutions.

Michigan Copper Deposits. The Michigan copper district has a recorded production of nearly 5 million short tons of copper metal. From a peak of 136,846 short tons of copper in 1916, output had waned to 21,812 tons in 1952. Although not an important supplier at present, this district warrants description because of past productivity, geologic environment, and unusual mineralogy marked by an abundance of native copper. Furthermore, the White Pine mine is a potential producer of chalcocite-bearing ores which may do much to revive the importance of the region in the future.

The Michigan copper district occurs as a belt along Keweenaw Peninsula. Here a thick accumulation of basaltic lava-flows with intercalated layers of conglomerate is bent to form a great syncline, and this major down-warp underlies the present basin of Lake Superior. The south limb of the fold contains the mining district and dips northerly under the lake. The mineralized section forms a belt about 100 miles long and from 2 to 4 miles in width. Its central part, about 26 miles in length, has supplied over 95 per cent of the district's production. Of the total copper, approximately 44 per cent was extracted from one great ore body, the Calumet conglomerate, and 49 per cent came from five so-called amygdaloidal ore bodies.

Three types of copper deposits are recognized, namely: (1) lode deposits along conglomerate beds, (2) lode deposits following amygdaloidal lava tops, and (3) fissure deposits. The latter have furnished less than 2.5 per cent of the district's production. Thus the important deposits of native copper occur in restricted sections of a few conglomerate horizons and in certain parts of a few amygdaloidal lava tops.

The great ore body in the Calumet conglomerate had produced approximately 58 million tons of ore up to 1925, which averaged about 2.5 per cent copper. This conglomerate is lenticular with a range in thickness from 5 to 20 feet. It has been developed for a distance of about 18,000 feet on strike and to a maximum depth of 9,300 feet down the 38-degree dip. Down dip this great lens becomes longer and thicker, grading out to sandy or shaly margins so that in longitudinal section it has the outline of an inverted funnel. Ore is confined to the conglomerate as though the ore-bearing solutions were unable to enter the marginal sandstone or shale and the solutions converged and were concentrated upward to deposit richer ore. Native copper in association with adularia, epidote, calcite, and quartz replaced the finer material between the pebbles of the conglomerate.

Ore bodies in the amygdaloidal flow tops have ranged between 0.6 and 1.5 per cent copper. These lodes average 13 feet in thickness and extend great distances laterally and down dip. The Kearsarge lode, for example, had produced (through 1925) 60 million tons at a little under 1 per cent copper. In the main productive area the thickness of lode extracted varied from 6.3 to 12.6 feet and was mined over a length of 6 miles. The Quincy lode has been followed 10,000 feet down its dip. In the amygdaloidal lodes, native copper is found in the vesicles in association with quartz, calcite, epidote, chlorite, adularia, sericite, pumpellyite, ankerite, and zeolites.

The fissure deposits are veins along fractures that strike parallel or across the beds. They have furnished only a minor amount of the total copper produced, although a few are noted for native copper occurring in large individual masses.

The ore body at the old White Pine mine contained native copper as the predominant mineral in a sandstone host rock. In the new mine, soon to be in production, the prevailing mineral is chalcocite, occuring principally in shale which has been folded, dragged, and faulted in places. The ore is found in four contiguous beds whose total thickness averages 16 feet. The deposit is 5 miles long and contains nearly 300 million tons of developed plus probable ore averaging about 1 per cent.

Bisbee, Arizona. The Warren mining district at Bisbee, Arizona, has furnished an output of around 2.25 million tons of copper along with substantial amounts of silver, gold, lead, zinc, and some manganese, all from within an area of approximately 4 square miles.

Although copper ore is abundant in both porphyry and limestone, in the past Bisbee has been particularly famous for its great deposits of so-called "limestone ore." It is an outstanding example of ore deposition centered upon and partly encircling a core of granitic porphyry, part of the latter, itself, also being ore.

Structurally the district is dominated by the Dividend fault, which strikes northwest. South of this break a large block of sediments, including a great thickness of limestone, has been fragmented and downdropped. Within this block sedimentary formations are distorted to form a shallow, elongated structural basin which pitches down to the southeast at a flat angle. Faults south of the Dividend strike predominantly northeast-southwest and are arranged with respect to it, in plain view, like the tines of a rake. A second group of faults is about parallel to the Dividend, but its members are less numerous.

The Sacramento Hill stock-like body of granite porphyry is symmetrically placed on the north margin of this faulted basin. On the south side of the Dividend fault the porphyry frays out into a complicated network of dikes, sills, and irregular bodies, some of which follow the more important faults to the south.

Disseminated ore of the porphyry copper type occurs within the Sacramento Hill intrusive body. Surrounding this, on the south side of the Dividend fault, ore in limestone is found as a great swarm of ore bodies arranged like a rude semicircular collar, beyond which ore follows out erratically along and between the major breaks. Ore in limestone has furnished most of the past production of the district; ore in porphyry is now developed for open-pit mining.

Most of the ore bodies in limestone have, or had before oxidation, a central core of pyrite and quartz carrying small amounts of copper around which abundant sulfides of copper and iron occurred. On the northwest, oxidation has obscured these relations, and it has cut down and shrunk the height of some ore bodies to give flat, tabular forms with oxidized or secondarily enriched ore. Toward the southeast, the height of the important ore bodies is at least as great as their length or width, and farther east height is generally greater than length or width. Away from the heavily mineralized central part of the district the ratio of zinc and lead to copper increases.

Some ore has been found in all of the Paleozoic limestones of the Bisbee district, but certain beds in certain sections carry more ore than those above or below them. There is a progressive change in what constitutes the favorable horizon when the district as a whole is considered, with ore being found in higher formations toward the southeast.

The Campbell ore body is one of the important deposits at Bisbee. It is an irregular plug-like body that is composed of a core of silica and pyrite surrounded by an irregular and discontinuous shell of copper ore. Near the borders of the ore, sphalerite and galena become more abundant.

Farther out, specular hematite is prominently developed and sulfides are scarce. The core itself carries low values in copper, gold, and silver. The vertical axis of this silica-sulfide mass is about 1,100 feet with horizontal dimensions of several hundred feet.

Bisbee ores were deeply oxidized, and for many years most of its copper came from deposits of this type. Nevertheless, rich secondary sulfide ores occur, and primary sulfides are found at greater depths eastward. Important sulfide minerals are pyrite, chalcopyrite, bornite, chalcocite, galena, and sphalerite, whereas malachite, azurite, cuprite, and native copper were abundant in the oxidized ores mined in the early days of the district.

Jerome, Arizona. The Jerome district contained two great ore bodies, those of the United Verde and United Verde Extension mines. The latter was worked out some years ago, and the other is now also exhausted.

The United Verde ore zone is dominated by a gigantic, very irregular, steeply plunging sulfide pipe which dies out at depth into scattered root-like prongs. It is found along a northeast-trending contact between quartz porphyry and diorite. In most places these igneous rocks are separated by a band of so-called "bedded sediments" and greenstone, but near the ore zone this band is mostly obliterated. The rocks associated with the mineralization are Precambrian in age and the time of mineralization has likewise been established as Precambrian.

The most abundant sulfide mineral is pyrite, and this makes up the bulk of the massive sulfide pipe. The principal copper-bearing mineral is chalcopyrite. Associated minerals of less importance are quartz, dolomite, sphalerite, tennantite, bornite, arsenopyrite, and galena. In general, chalcopyrite is sparingly distributed in the massive sulfide to provide a very lean copper content. In special situations it occurs abundantly to form the ore bodies for which the mine is famous.

The massive sulfide pipe has been followed from near the surface down to about where it pinches out near the 4,500-foot level. On upper levels, a plan view exhibits a rudely lenticular outline; lower down it appears as an irregular crescent; at still greater depths elements of the crescent split apart and additional detached bodies appear; on lowermost levels this splitting apart increases, the mineralized zone narrows, and sulfide mineralization goes down in the form of scattered root-like prongs. On upper levels, the massive sulfide has an average extent in plan of about 6 acres. This body is surrounded by a highly irregular border of "black schist" characterized by the very abundant development of black chlorite both in quartz porphyry and probably also in rocks of the greenstone group.

On upper levels, many ore bodies are found within the massive sulfide;

at greater depth they are more closely confined to its footwall margins and to the black schist; with added depth more ore appears in the flanking porphyry, either associated with detached bodies of black schist or in porphyry free from black schist alteration. About one-seventh of the volume of the mineralized zone was commercial copper ore.

The United Verde Extension ore body does not crop out, being covered by 500 to 700 feet of overlying lava, limestone, and sandstone. It is found about 7,000 feet east-southeast from the outcrop of the United Verde, on the hanging-wall side of the Verde fault.

The United Verde Extension exhibited an extensive leached zone underlain by rich secondary chalcocite to a depth of 150 feet. Below this, partly enriched ore continued for another 300 feet before primary sulfides were reached. The latter were comparable in character to those of the United Verde ore body.

The intensity and extent of secondary enrichment in the United Verde Extension mine formed an outstanding body of supergene chalcocite that placed the mine in the front rank of high-grade copper producers. Nevertheless, oxidized copper minerals were prevalent throughout, and in some of the higher horizons of the mine accounted for over half the copper content of the ore.

Kennecott, Alaska. The famous copper deposits at Kennecott are now worked out and the mines abandoned. The ores were extremely rich masses of digenite, chalcocite, and covellite in dolomite unaccompanied by the usual pyrite, quartz, and other introduced gangue minerals. Sulfides made up from 10 to 100 per cent of the ore. The Jumbo Main vein carried a chalcocite body 80 feet wide, 150 feet long, and 400 feet down dip that averaged over 60 per cent copper.

Superior, Arizona. The principal vein-like zone of the Magma mine at Superior cuts through inclined sediments and diabase sills and contains several distinct shoots separated by barren vein material. Where the vein walls are diabase, ore deposition is stronger than where sedimentary rocks form one or both walls. The principal ore minerals are pyrite, bornite, chalcopyrite, and enargite with subordinate tennantite and primary chalcocite. Ore shoots are bordered by zinc ore. The mine produces copper, silver, gold, and zinc.

Globe, Arizona. A somewhat similar ore occurrence is found 20 miles east of the Magma mine, where the productive copper mines at Globe were formerly operated. Ore bodies of the famous old Dominion mine were developed over a length of 3 miles and to a depth of 0.5 mile along a complicated fault zone. Ore occurred in shoots along this zone, but, in contrast to the Magma mine, there was a notable improvement where brittle sedimentary rocks formed the walls. Primary ores carried pyrite, chalcopyrite, and bornite; enriched zones exhibited secondary chalcocite; oxidized ores contained malachite and chrysocolla with subordinate amounts of cuprite, azurite, and native copper.

Ducktown, Tennessee. At Ducktown, copper deposits have the form of roughly tabular masses, some of which are curved, lens-shaped, or folded. The ore beds containing these bodies are parallel to the strike of folded schists, and the ore bodies themselves are approximately conformable to the structure of the country rock. Much of the ore is almost massive pyrrhotite and pyrite with subordinate chalcopyrite and minor amounts of sphalerite, bornite, and other minerals. The various ore lenses range in size up to 300 feet wide and 3,000 feet long. The Burra Burra mine is on the most continuous vein and has been opened to a depth of 1,800 feet. The district supplies copper and sulfuric acid from ores that carry about 1.5 per cent copper. A thin, enriched chalcocite zone occurs below the gossan.

Sedimentary Copper Deposits. In the western United States (particularly in Utah, Colorado, Arizona, Texas, and New Mexico), as well as in other parts of the world, ores of copper along with other metals are found disseminated in sandstones and shales distant from igneous rocks. The sedimentary strata containing such ores are usually parts of a thick series of beds deposited in shallow water, and the series as a whole is commonly of reddish color. These are the so-called "sedimentary copper deposits" occurring in the stratigraphic group known as the "Red Beds," although the particular layers that they occupy are seldom of red color. Such deposits have widespread distribution, but the ores are of generally low tenor and only certain richer deposits have been mined. Important minerals are chalcocite, roscoelite (a vanadium mica), and various copper and lead vanadates; bornite, chalcopyrite, galena, and pyrite are less common. One theory of origin holds that these ores have been concentrated by surface waters which collected copper that had been deposited with the sedimentary beds when they were laid down.

Canadian Copper Deposits

Although now occupying fifth place in world copper production, Canada obtains most of its copper from ores in which the principal or a substantial value is carried by other metals. About 45 per cent of Canadian copper comes from nickel-copper ores and the remainder from gold-copper, copper-zinc, and copper-lead-zinc ores.

Copper minerals are found in every province of Canada and in many parts of the Northwest Territories, although principal production has been confined to Ontario, British Columbia, Quebec, Manitoba, and Saskatchewan, in that order.

Sudbury, Ontario. The important Sudbury mines are found near a large intrusion of norite-micropegmatite 36 miles long and 26 miles wide. This crops out as a great ellipse, and for many years these nickel-copper ore deposits were considered to be classic examples of origin by "magmatic segregation" whereby the sulfides had settled out and collected along the underside of the intrusive as it cooled and crystallized. However, this view is now seriously challenged, and an origin due to replacement by hydrothermal solutions is favored by many.

The Sudbury norite-micropegmatite has invaded a group of Huronian formations; later than the norite-micropegmatite are the Murray and Creighton granites. Following these are younger trap dikes, breccia, and olivine diabase dikes. These are succeeded by faulting, after which ore deposition took place.

The time of intrusion of the quartz diorite, which is believed to be related to the norite and is the principal host rock, is not clear; however, ore always occurs within quartz diorite or not far from it, although all of the quartz diorite, of course, is not productive. Channelways for ore-bearing solutions and sites of deposition for ore are provided by faults, well-defined breccia zones, and indefinite areas of shattering and brecciation; wherever any of these intersect the quartz diorite, mineralization or an ore body is likely to occur.

Nickel-copper ores of the Sudbury district are of the sulfide type containing pyrrhotite, chalcopyrite, pentlandite, minor cubanite, complex arsenides, a nickel-bismuth sulfide (parkerite), tellurides of gold and silver, sperrylite, and platinum-group metals. Various other minerals in minor amounts are also noted. There are three textural varieties of ore, all of which are made up of essentially the same minerals to give: (1) a typical disseminated ore with sulfides scattered through quartz diorite; (2) a massive sulfide type in which sulfides in various kinds of rock breccias make up 60 per cent of the ore; and (3) a stringer type with an intricate pattern of veinlets in shattered and brecciated host rock.

Most of the Sudbury deposits are found near the margins of the norite intrusive. The most productive group, made up of the Creighton, Frood, Garson, Murray, and Falconbridge mines, lies on the south rim; a few others, including the Levack, are situated on the north.

The *Creighton mine* exploits a group of individual ore bodies. Here a slab of quartz diorite is intersected by a series of faults, and massive sulfide ore occurs along the faults and nearby in their brecciated footwalls. Heavily disseminated sulfides make ore near the faults, but fade on going away from them.

At the *Frood mine,* the Frood-Stobie ore body is found within a large dike-like zone of breccia. It is composed of two types of ore: (1) one is a dissemination of sulfides in quartz diorite, and (2) the other is a sulfide replacement of breccia matrix surrounding the quartz diorite ores.

Deposits in the *Garson mine* resemble those of the Creighton in that ore deposition is controlled by quartz diorite cut by a series of faults; structural control of ore deposition at the *Murray mine* is similar, although faulting is less conspicuous.

The *Falconbridge deposit* is composed of breccia ore, massive ore, and disseminated ore along a steep contact shear zone that involves norite, quartz diorite, and greenstone.

In the *Levack mine* on the north rim, ore is found associated with an irregular body of granite breccia intruded along the norite-gneiss contact. In the gneiss, ore is found as stringers and veins of massive sulfide; in the granite breccia, ore is mostly of the disseminated type.

Britannia, British Columbia. The Britannia area, some 20 miles north of Vancouver, is underlain by metamorphosed sediments and volcanic rocks that form a roof pendant in the Coast Range batholith. The ore bodies, eight of which have been discovered, occur as stringer-lodes, or as massive replacements, or as a combination of these two types in a sheared part of the pendant. Favorable host rocks are chlorite and sericite schists; the principal sulfides are pyrite and chalcopyrite, although abundant sphalerite is found in some sections. Copper, zinc, cadmium, gold, and silver are produced along with a pyrite concentrate.

Copper Mountain, British Columbia. The Copper Mountain deposit is a variety of a small porphyry copper and was mentioned in a foregoing section.

Rouyn, Quebec. The Rouyn district in northern Quebec contains the important Horne mine. Here massive sulfide ore is found in the faulted nose of a large, nearly vertical drag fold. Numerous tongues of diorite occur within and above the ore, which consists of pyrrhotite-pyrite bodies with cores and fringes of chalcopyrite and minor sphalerite and magnetite. Some 24 sulfide lenses are known and these replace dacite breccias and tuff. Besides the copper-bearing lenses, rich siliceous gold-quartz veins also occur and both gold and copper are produced.

Generally similar but smaller deposits are found in the nearby Aldermac, Normetal, and Waite-Amulet mines. The latter two also produce zinc and silver.

Flin Flon, Manitoba-Saskatchewan. Near the Manitoba-Saskatchewan interprovincial boundary are the Flin Flon and Sherritt Gordon mines. At the Flin Flon mine, ore is associated with quartz porphyry along a contact between lava flows on one side and pyroclastics and flow breccias on the other. The ore is found in six large lenticular to irregular bodies within a zone 500 feet wide. These bodies average about 900 feet long, 70 feet wide, 1,500 feet in vertical depth, and 2,500 feet in length along the plunge. Seventy per cent of the ore is of the solid sulfide type, but disseminated ore occurs on the footwall side and along the bottom of the plunge of the heavy sulfide bodies. The ore consists of an intermixture of iron, zinc, and copper sulfides, among which pyrite is very abundant. Zinc, copper, cadmium, gold, silver, selenium, and tellurium are recovered.

Sherritt Gordon, Manitoba. At the Sherritt Gordon mine, ore is found in two tabular sulfide deposits in metamorphosed sediments. The ore is coarse-grained and varies from massive to disseminated. Sulfides present are principally pyrite, pyrrhotite, chalcopyrite, and sphalerite. Copper, zinc, silver, and gold are produced.

Lynn Lake, Manitoba. At Lynn Lake, three ore bodies carrying copper and nickel have been found within a stock-like intrusion of dioritic rock.

Copper Deposits of Mexico

Most of the important Mexican copper deposits are found in the State of Sonora not far south of the Arizona border.

Cananea, Sonora. The most productive of the Mexican copper deposits are in the Cananea district. Here bedrock consists of quartzite and limestone overlain by a thick series of volcanic flows, the whole intruded by granitic rocks, diabase, and quartz porphyry. Ore bodies occur as limestone replacement deposits along bedding and contacts, as disseminated deposits in volcanics and porphyry, and as "breccia pipes." The important deposits are found as approximately vertical pipe-like structures that pierce various host rocks and may be overlain by disseminated deposits. The most outstanding of the pipe-like bodies was the Colorada. This apexed on the 500 level as a ring-shaped deposit that increased to 600 feet in length and 500 feet in width on the sixth level. The ring converged downward and became a solid ore pipe at the tenth level. The sulfides consisted of bornite, chalcopyrite, and molybdenite with minor pyrite, tennantite, covellite, and chalcocite. This superb deposit is now exhausted, and current production comes largely from other ore bodies nearby.

Boleo, Baja California. The unusual Boleo deposits in Lower California are made up of three "clay ore" beds 1 to 4 meters thick that occur in marine tufaceous sediments. The ore contains chalcocite with minor bornite and chalcopyrite and averages 2.5 per cent copper.

Nacozari, Sonora. The Pilares mine at Nacozari produced copper from

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a pipe-like body of andesite and latite breccia. Pyrite and chalcopyrite are the principal sulfides below an enriched zone carrying secondary chalcocite to a depth of 200 feet.

Copper Deposits of the West Indies

Matahambre, Cuba. Cuba is the only important copper producer in the West Indies. Here copper was first mined when Juan Espinosa opened the El Cobre mine in Oriente Province in 1532. However, the most productive deposits, those of Minas de Matahambre near the western end of the island, were not discovered until 1912.

The Matahambre deposits consist of rude pipes and thick vein-like bodies with a high degree of irregularity. The vein-like zones shorten with depth and become pipe-like on lower levels. The assemblage of ore bodies is that of a complicated cluster confined to a relatively small area of structural favorability, going down over a half-mile at depth into converging prong-like roots. These copper deposits are unusual in that they occur in a thick series of sandstone and shale with no igneous rocks nearby; however, the ore bodies appear to be genetically related to a prominent shear fault that knifes down deeply to a possible sourceway.

Matahambre ore bodies consist predominantly of primary chalcopyrite, pyrite, and quartz. Bornite appears locally, and other minerals, such as pyrrhotite, sphalerite, galena, calcite, ankerite, and siderite are sparsely present. Chalcopyrite occurs as fillings in fractured rock and between breccia fragments and is also found to replace fragments and walls. All gradations are found between reticulated veinlets of ore minerals and masses of solid chalcopyrite. Mineralization is associated with widespread chloritization and with a number of brecciated zones carrying quartz in thin reticulated veinlets.

Other Copper Deposits of South America

The fact that most of the important South American copper deposits were included in a foregoing section on the "porphyry coppers" should not detract from the importance of this continent as a supplier of copper. In 1952 South American mines yielded 484,154 short tons of copper, or about 16 per cent of world production. Most of this, of course, came from the porphyry copper deposits of Chile, but the ore bodies of Cerro de Pasco and Morococha, Peru, are important and deserve brief descriptions.

Cerro de Pasco, Peru. At Cerro de Pasco, a body of heavy pyritic material over 5,000 feet long with an average width of about 400 feet and a depth of 1,400 feet occurs along the eastern and southeastern side of an old volcanic vent. Primary copper ores carrying enargite are found as irregular shoots with gradational boundaries in the pyrite body and as various veins transverse to the northerly trend of the mineralized zone. Parts of the pyrite body also contain galena and sphalerite and constitute lead-zinc ores, and pyritic silver ore occurs as a broad mass at the south end of the zone.

A group of strong veins striking easterly is also found in altered shales south of the heavy pyrite. Eastward the mineralized zone contains tabular deposits replacing limestone beds with flat easterly dip. These are mostly oxidized and only locally carry a little copper.

Secondary sulfide ores rich in chalcocite were the principal source of copper for many years at Cerro de Pasco, but production from them has gradually diminished. The chalcocite ore bodies usually lie just below the bottom of an oxidized crust locally called "pacos." This is siliceous silver-bearing material derived from the oxidation of sulfide deposits and varies in thickness from a few feet to several hundred. Parts of the pacos carry enough silver to warrant mining them for converter flux.

Cerro de Pasco ore deposits yield copper, lead, zinc, silver, gold, bismuth, cadmium, and arsenic.

Morococha, Peru. At Morococha, beds of limestone and volcanic rocks are intruded by irregular stock-like bodies of diorite and quartz monzonite from which extend satellitic dikes, sills, and tongues. Ore occurs in a series of east-west veins in limestone, volcanics, and quartz monzonite and also in an erratic group of so-called "manto" deposits arranged along limestone bedding.

The principal metalliferous minerals at Morococha are pyrite, chalcopyrite, enargite, magnetite, silver-bearing tennantite-tetrahedrite, sphalerite, and galena along with a number of rarer minerals. Quartz is the most common gangue material.

Morococha exhibits a pronounced zonal arrangement of metals and minerals, both horizontally and vertically, and the zonal arrangement, along with other features, suggests that the source of the ores was the quartz monzonite magma chamber.

Corocoro, Bolivia. At Corocoro, native copper occurs in a series of sandstone beds where the host rocks are much lighter in color than the prevailing deep-red sediments. The ores grade upward into a chalcocite-covellite-domeykite zone.

Copper Deposits of Europe

Bor Mines, Yugoslavia. The Bor copper mines are reported to be among the largest in Europe. Here ore is found as three massive bed-like deposits in altered andesite porphyry. The largest contains pyrite and enargite with minor amounts of luzonite and famatinite. The ore, enriched by secondary chalcocite and covellite, carries from 5 to 6 per cent copper along with some gold. The second ore body also furnishes 5 to 6 per cent ore, and the third carries pyrite and chalcopyrite with a copper content of 1 to 2 per cent.

Outokumpu, Finland. The Outokumpu ore body is one of the largest individual copper deposits of Europe. Sulfide ore occurs in a brecciated zone in quartzite to form a body in the shape of a long plate. The deposit is 6 to 14 meters thick, 300 to 400 meters wide, and at least 3,700 meters long. The breccia fragments are cemented by chalcopyrite and pyrrhotite and are impregnated by pyrite and chalcopyrite. The tenor is 3.14 per cent copper and about 25 per cent sulfur with small amounts of zinc, silver, and gold along with some nickel and cobalt. Reserves are currently reported at 18 million tons of ore.

Boliden, Sweden. Copper production in Sweden is dominated by the great ore body at Boliden. Here a steep lens in schist was found in 1923 by geophysical prospecting. It contains quartz, pyrite, fine-grained arsenopyrite, pyrrhotite, sphalerite, and chalcopyrite. Bismuth minerals along with tetrahedrite and galena are also present. This deposit is reported to contain 13 million tons with a tenor of 1.20 per cent copper. It also carries important amounts of gold, silver, arsenic, and sulfur.

Norway. In Norway, copper is found in a considerable number of small deposits: (1) where copper is the main product of economic value, (2) where copper occurs in pyritic ores whose sulfur is also recovered, and (3) where copper is a by-product of sulfide nickel ores. The more important deposits are generally in the form of flattened fish-like lenses, although in some cases they may take the form of pencils. These ore bodies contain pyrite and pyrrhotite with varying amounts of copper.

Huelva District, Spain-Portugal. The pyritic ore bodies of the Rio Tinto or Huelva district of Spain-Portugal are the oldest worked and the most important copper-sulfur deposits of the world. These are enormous lenses of pyrite carrying from 0.3 to 3.0 per cent copper in the form of chalcopyrite, with a little chalcocite and covellite in a shallow enriched zone. Also present are minor amounts of sphalerite and traces of uncommon arsenides, selenides, and antimonides. From the ores are produced sulfur and copper; a little lead, zinc, gold, and silver; and small amounts of nickel, cobalt, and other metals. Going to treatment are smelting ore, leaching ore, copper-sulfur ore, and sulfur ore. Bateman reports that the Rio Tinto district has produced over 200 million tons of pyrite ore and 5 million tons of copper metal with as much remaining in reserve.

The Rio Tinto deposits occur as great lenses of solid sulfide (with only

1 to 5 per cent of accompanying silicates) bordered by disseminated sulfides. The ore bodies are associated with quartz porphyry intrusives in slates and are elongated east-west parallel to the structure of the region. They are widely distributed in a long, narrow zone, although the more important deposits are more localized in groups within the zone in *en echelon* arrangement. Most of the lenses vary between 300 and 700 meters in length and between 50 and 150 meters in width; those with the largest surface outcrop appear to reach the greatest depth, which may be as much as 550 meters. Certain of the lenses are longer, and three of them, essentially continuous, have a combined length of 3,000 meters. Throughout the district, some 50 ore bodies have been exploited, mostly by means of large open-cuts. These deposits were formed at different horizons, and erosion has destroyed some, exposed others, and has probably not reached additional bodies still remaining hidden.

Mansfeld, Germany. The famous copper-bearing shale (Kupferschiefer) of Mansfeld, in central Germany, has been the principal copper producer of this country since A.D. 1150. Here ore occurs in a thin but widespread bed of black organic shale, about 50 centimeters of which is utilized as ore. This consists of sulfides minutely distributed through the shale. Bornite predominates and is associated with chalcocite, chalcopyrite, galena, sphalerite, and tetrahedrite. Small quantities of silver, nickel, cobalt, selenium, vanadium, and molybdenum are also present. The ore minerals make up about 12 per cent of the bed. The origin of the ore bed has occasioned much controversy. A syngenetic, sedimentary origin has been much favored, although there is compelling evidence for a hydrothermal origin.

Cornwall and Devon, Great Britain. Although no longer an important contributor, during the first half of the nineteenth century, Great Britain produced more than half of the world's copper ores, and most of these came from mines in Cornwall and Devon. Here a mineralized belt traverses the peninsula for 70 miles and is generally about 8 miles wide. Copper ore occurred sporadically along this zone in veins cutting slates, phyllites, and locally granite. Downward, copper was associated with tin, but upward it was found in a zone of mixed sulfides of copper, zinc, and lead.

Copper Deposits of Russia

The last fairly informative account of Russian copper deposits was published in 1935. For the year 1934, production from these deposits amounted to about 49,000 short tons of metal. By 1937 this production was approximately doubled, and it continued to rise to an amount estimated at 300,000 to 320,000 tons for 1952. Although doubt has been expressed regarding such a substantial increase, nevertheless, it would appear that exploration and development have undergone considerable expansion and that there is much to be added to the brief account that follows.

Copper deposits in Russia are numerous but are widely scattered over a vast expanse of country. A number of types are represented, including copper-nickel deposits, contact-metasomatic deposits, hydrothermal deposits, and sedimentary copper deposits. In the hydrothermal group are massive pyritic replacement bodies, vein deposits, impregnations in sandstone, and deposits of the porphyry copper type. Copper is found in such widely separated regions as the Kola Peninsula on the northwest, the Ural Mountains and Novaya Zemlya Island, the Caucasus and Transcaucasia on the southwest, the Kazak Steppe and Altai in northeastern and eastern Kazakstan, the Transbaikalia and Far Eastern Region toward Manchuria, and various other localities.

Copper-nickel deposits, stated to be of magmatic origin, are found in the Kola Peninsula and the Norilsky region of western Siberia. These contain pyrrhotite, chalcopyrite, and pentlandite forming low-grade disseminations or small aggregated bodies with a copper content of 1 to 4 per cent, 0.5 per cent or less of nickel, and some platinum-group metals.

Contact-metasomatic deposits are found in the Ural Mountains, Kazakstan, and Central Asia associated with granodiorite intrusive rocks.

Lodes of cupriferous massive pyrite, said to be similar to the Rio Tinto type, are reportedly common in the Ural region, where some 100 deposits are known. Ore shoots range in length from 50 to 600 meters with a copper content varying from 1.4 to 2.7 per cent. Reserves are stated to be large.

Sulfide impregnations in sandstone, the so-called Djeskasgan type, are reported from Kazakstan and are claimed to be similar to the Rhodesian type, although comparable continuity is not apparent from descriptions given.

Numerous deposits of the porphyry copper type are reported to be present in Kazakstan, the Altai, Central Asia, in Transcaucasia, in the southern Urals, and in southern Tadjikistan. Although considerable reserves are claimed, their true importance as producers by large-scale methods cannot be determined from available descriptions.

"Red Beds" of Permian age in the Ural Mountains and the Don Basin carry thin sandstone layers 4 to 16 inches thick with disseminated copper minerals that give an average tenor of 1.5 to 1.9 per cent copper. Comparable mineralization is found in "Red Beds" of Silurian age in the Lena region.

Copper Deposits of Asia

Japan. Japan produces copper from numerous small mines. These exploit replacement deposits, fissure deposits, and a few contact-metasomatic deposits.

The so-called Besshi type of deposit is the most productive in Japan. These are massive, pyritic replacements of green schist. They are tabular in form and approximately conformable to adjacent stratification. Sulfide minerals present are pyrite, pyrrhotite, chalcopyrite, and sphalerite. Most of the ore bodies contain less than a few hundred thousand tons, but they commonly occur in clusters; on the other hand, a deposit of unusual size, the Besshi, has produced 19 million metric tons averaging 3.8 per cent copper and has been worked since A.D. 1691. A second type of replacement is known as "black ore"; such deposits contain galena, sphalerite, chalcopyrite, and pyrite replacing tuffs or shales. Besides the above, a large number of productive Japanese mines obtain copper from fissure veins. This vein ore usually carries chalcopyrite accompanied by pyrite or pyrrhotite, and all of the copper-bearing veins are associated with acidic or intermediate igneous rocks. In addition, contact-metasomatic copper deposits are widely distributed in Japan, but only a few have been productive.

Cyprus. At Skouriotissa on the Island of Cyprus, copper is obtained from large pyrite lenses. Mining was carried on here in ancient times, and the English word, copper, was derived from the Greek name of the island, Kypros, through the Latin *cuprum*. The old mines lay idle for 17 centuries, but ore bodies were discovered in 1914 and the ancient industry was re-established along modern lines.

Turkey. The copper deposits at Ergani are the principal producers of Turkey. Here a massive pyritic body of roughly elliptical shape occurs between serpentine and diabase. Copper is contributed by chalcopyrite and secondary covellite. Below the massive pyrite is disseminated ore in chloritized diabase carrying pyrite, magnetite, chalcopyrite, and covellite with minor chalcocite and sphalerite. Reserves are stated to be 2.25 million metric tons of pyritic smelting ore with 9.07 per cent copper and 0.4 per cent cobalt plus 1 million tons of concentrating ore with 4 to 5 per cent copper.

Philippine Islands. The Lepanto mine is the most important supplier of copper in the Philippine Islands. The ore body is a large tabular deposit standing steeply with a thickness of approximately 200 feet, but its length and width are as yet not fully determined. The predominant sulfide minerals are enargite, pyrite, and minor chalcopyrite, which are found as replacements and fillings of fault breccia in silicified andesite.

Ore reserves are about 2 million tons of 4.19 per cent copper with 0.14 ounces gold and 0.65 ounces silver per ton.

India. In India the most important copper ore deposits are found in Singhbhum, Sikkim, and Bawdwin. In Singhbhum district, the ores occur as indefinite lodes with chalcopyrite and pyrite interbedded with phyllites and schist. In the small State of Sikkim, numerous veins have been discovered containing ores of copper, lead, and zinc. In Burma, copper ore is found in portions of the Bawdwin silver-lead-zinc mine.

China. Copper is reported to be widely distributed in China, occurring in almost every province. The ore bodies of importance, however, are limited to five regions: Southern Manchuria, the southeastern coastal region, the Yangtze Valley, the southwestern region, and Sinkiang province. A variety of deposits are known to exist, but in many places development has not been sufficient to determine their worth. Reserves in terms of metal are of the order of 2 to 3 million tons; current mine output is about 3,000 tons.

Other Copper Deposits of Africa

Little Namaqualand. The Little Namaqualand region of northwestern Cape Province, Union of South Africa, has been an active copper producer during most of the past century. Here complex swarms of noritoid dike-like bodies of limited length intrude Precambrian paragneiss, and a number of these intrusives have provided copper for a thriving mining industry. The "dikes," when viewed in cross section, are blunt-ended on the upper, or leading, edge, and they wedge out at depth to narrow roots. Thus they are encased in gneiss both above and below as well as on their sides. Copper ore bodies are found in an upper bulge of certain "dikes" below the roof of gneiss and above the constricting root. Mineralization is primary and of several kinds: (1) dominantly bornite with subordinate chalcopyrite; (2) dominantly chalcopyrite with subordinate bornite; and (3) chalcopyrite with abundant pyrrhotite. These types are further subdivided into disseminated and massive varieties. Ore bodies being currently mined vary in tenor from 2.2 to 5 per cent copper. These "headed dikes" and their contained ore are found at various horizons and have undergone various degrees of denudation, some being nearly destroyed, others being medially truncated, and still others remaining deeply buried. The size of the better Namaqualand ore bodies generally ranges between 0.5 and 9 million tons. A magmatic origin was early proposed and is still seriously entertained, although there are points on which it is challenged.

Messina, Transvaal. The Messina copper mines, in the northern Transvaal, Union of South Africa, exploit three producing sections at

Messina, Harper, and Campbell. The ore is localized along a persistent zone of fissuring where the major copper ore bodies are found in fractured rock near the contact of granite gneiss and quartzite. Chalcopyrite, bornite, and chalcocite are the predominant copper-bearing minerals.

Tsumeb, South West Africa. Copper in the form of tennantite, enargite, chalcocite, and bornite is associated in substantial amounts with lead and zinc in massive vein-like replacements and disseminations in dolomite at Tsumeb, in the Mandated Territory of South West Africa.

Copper Deposits of Australasia

The principal producers are the Mount Morgan gold-copper deposit in Queensland and the Mount Lyell ore bodies in Tasmania.

Mount Morgan, Queensland. At Mount Morgan, an irregular ore deposit occurs in sandstone and cherty rocks surrounded on both sides by intrusive granite. Below a surficial oxidized zone carrying silver, primary ore is found containing pyrite and chalcopyrite with 2 to 3 per cent copper and considerable gold.

Mount Lyell, Tasmania. At Mount Lyell, ore bodies are found in a shear zone along the side of a porphyry dike. They appear as two types: (1) great lenticular bodies of pyrite, and (2) mineralized bands of schist. The Mount Lyell pyritic body is elliptical in form, being 800 feet long and 200 feet wide at the surface and tapering gradually to its base at a depth of about 730 feet. A number of other ore bodies occur in mineralized bands of schist. Their ore consists of schist or quartzite with bornite, chalcopyrite, and pyrite. Mount Lyell reserves of low-grade material are substantial.

Résumé

The foregoing description of copper deposits is not complete, but it serves to give a view of (1) the more important copper mines and productive districts; (2) the great variety of deposits and geologic conditions under which they occur; and (3) something of the geographic and political distribution of present sources of copper.

Copper ores are found in a great variety of host rocks, such as granite, monzonite, diorite, and their porphyritic equivalents; also in norite, diabase, quartz porphyry, andesite, basalt (trap), conglomerate, sandstone, shale, limestone, dolomite, quartzite, gneiss, and numerous kinds of schist.

In form, copper deposits include bodies variously called blankets, beds, mantos, inclined and flat tabular bodies, lenses, veins, stockworks, pipes, pencils, and plugs.

Copper deposits may be (1) widely distributed through zones of great length (Northern Rhodesia-Belgian Congo); (2) rather closely grouped within parts of an extended zone (northern Michigan); (3) scattered over a large region, apparently related to a grand structural arrangement (western and southwestern United States); (4) concentrated in a swarm of veins in a limited area (Butte, Montana); (5) grouped to form an individual district where copper occurs within and hugging the periphery of a porphyry stock (Bisbee); (6) located in great pipes or lenses where massive pyrite is impregnated with copper-bearing minerals (Jerome, Arizona, and Rio Tinto, Spain); (7) spread over great areas with copper minerals erratically disseminated in sandstone ("Red Bed" deposits); or (8) concentrated sharply in very rich deposits (Kennecott, Alaska).

In output, the more important of the individual copper deposits furnish from several hundred thousand short tons of ore per year to over 30 million tons annually.

Reserves and Future Discoveries

The world's reserves of copper ores, and particularly those of the United States, are being rapidly depleted. The United States is by no means a "have-not" nation in respect to this commodity, and the world's copper reserve, as now known, will not be exhausted for many decades, but the present pattern of increasing uses for copper and the proportion of known reserves needed annually to supply this demand are matters of concern. Although precise figures are not available, approximately 180 million tons of copper ore are currently being mined in the world each year (of which about half comes from mines within the United States). This world figure is about equivalent to the annual depletion of a great ore deposit carrying 1.65 per cent copper per ton. Obviously, if current reserves are to be maintained, on the average an immense ore body must be made available each year, or the aggregate of annual increases in reserves of producing mines must reach this figure. This is becoming increasingly more difficult to accomplish.

Copper ore reserves may be augmented in several ways: (1) by extension of known ore bodies or districts with the finding of additional ores of comparable tenor to the "original" ore bodies; (2) by improving methods of mining and beneficiation, or by increase in the price of copper, so that low-grade copper-bearing material already known can be profitably handled; (3) by finding extensions and new bodies of low-grade ores that could be profitably mined and treated only under these improved conditions; and (4) by the discovery of new ore deposits and districts containing the richer ores.

In the past, most of the copper deposits have been found in areas where bedrock is exposed to view or where there is only an intermittent cover of soil and vegetation. In such regions, surface indications of copper are commonly displayed by brightly colored blue and green oxidized copper minerals. These showings were followed downward and outward by means of mining excavations and boreholes, and many important deposits and districts were thus developed.

Where a region is more regularly blanketed by soil and vegetation, discovery of copper deposits is naturally more difficult, even though the cover is relatively shallow. This is the case in the Northern Rhodesian copper belt, where a very limited display of copper-stained cropping was responsible for its initial discovery, but skillful use of geological structure and projection led to the vast reserves that have been outlined in a region of sporadic outcrops.

Because of the location of several important copper deposits near the edges of areas blanketed by thick deposits of younger sediments or lava flows, it seems reasonable to believe that certain regions with deep cover may contain hidden copper deposits. These will be difficult to bring to light, and their discovery must await the development of special methods of search.

It is expected that new copper ore bodies will be found in the several environments described above, although it is not assured that such discoveries will keep pace with demand. Inasmuch as the areas of exposed bedrock in the western world have already received considerable attention, it appears that vast areas of northern Asia should be searched by modern techniques if copper is to be found where bedrock is open to inspection. Where cover is shallow but extensive, currently available and future improved geophysical and geochemical methods must be employed to supplement geologic patterns and projections. Where cover is deep, geophysical observations in drill holes and other geophysical methods yet to be developed offer possible means of attack. Where the cover is an integral part of the bedrock, a buried formation, intrusive body, or structure may be selectively replaced by copper minerals at depth without a tempting amount of copper leaking into rocks exposed at the surface. In this situation, geologic structure along with geophysical observations may indicate the deeply buried mineralized zone, and this method is now being successfully used by a few organizations.

Thus it is evident that continued discovery of copper demands that exposed sections of the earth be carefully searched and that various methods—geological, geophysical, and geochemical—be more fully developed and used for the covered sections. Whereas discoveries in the past were made mostly by prospectors, many future discoveries will depend upon specialized scientific techniques used in conjunction with deep exploration, all at considerable expense.

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Chapter 3

The Concentration of Copper Ores

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Copper occurs in nature principally in the form of minerals of specific chemical composition and physical properties intimately admixed with rock-forming minerals of little or no commercial value. Native copper is also fairly common, mostly as small flakes and irregular particles, but occasionally as nuggets and large masses. On the average, the size of the individual copper mineral particle is seldom much greater than 0.05 inch and it is usually necessary to break down the rock to a fine sand passing a 48- or 65-mesh (Tyler) screen in order to effect physical liberation of these particles. This is the first step in any concentration scheme. If a chemical leaching method is used, however, much coarser crushing, say to ¼ or ½ inch, may be tolerated, because the solvent can diffuse through the minute channels in these larger fragments.

Broadly speaking, copper ores may be classified as sulfide ores and oxidized ores, though it is quite usual to find oxidized surface deposits grading into sulfide ores at depth. The presence of native copper is not unusual in both classes of ores, especially as a small proportion of the total copper, in which case it is handled by conventional concentration methods; if in greater amount and in coarse form, as at Calumet & Hecla in Michigan, special methods of concentration are employed.

Concentration is a general term used to cover the various physical methods employed to separate the unwanted waste minerals from the copper minerals in the ore to enrich in copper content the product to be smelted. This operation may also include the separation of the copper minerals from other valuable minerals such as those of lead or zinc, which are separately recovered in marketable form.

In the case of any given ore deposit, the most suitable treatment method will depend, of course, on both technological and economic considerations, but in general sulfide copper ores are treated by concentration, smelting, and refining methods, while oxidized copper ores are more commonly leached without concentration. In rare cases the ore as mined is of high enough grade to smelt direct without concentration.

Mining and Delivery of the Ore

Concentration of a sort actually begins in the mining of the ore, where every effort is made to deliver to the mill only rock from the copper-bearing zones of the ore body. If it becomes necessary for structural reasons to mine waste rock, it is kept separate from the ore and dumped on waste rock piles, or used for filling mined-out areas. Selective mining may also be practiced where it is economically sound to maintain a certain minimum grade (*i.e.*, copper content) in the ore passing to the mill, in which case the practice is to leave in place, or mine as waste, any rock showing a value below this cut-off point. Hand-sorting of sulfide ores is not practiced in North America, but there are mines in the Belgian Congo where massive, high-grade sulfide ore is hand-sorted from the mill feed for direct reduction in blast furnaces.

The average copper content of the ore delivered to the mills in North America is probably no higher than 1.25 per cent copper, and in certain large operations, such as at Utah Copper, less than 1.0 per cent copper. This has necessitated the handling of very large tonnages (10,000 to 20,000 tons or more per day) in order to reduce the costs per ton of ore treated. Utah Copper Company, with two mills each of maximum daily capacity of about 50,000 tons, and Phelps Dodge, Morenci, at 60,000 tons, are unique in being the largest operations of this kind in the world today.

Crushing

Referring to Figure 3-1 it will be seen that the first step in concentrating a typical copper ore is "coarse crushing" of the ore as it comes from the open-pit or underground mining operation. These primary crushers are preponderantly of the gyratory type and built in very large units capable in some installations of handling single pieces of rock of 60-inch dimension and weighing upward of 10 tons.

The gyratory crusher consists of a circular shell of cast steel, lined with manganese steel or other tough alloy steel, with the inner sides inclined toward a central orifice. A heavy shaft passes vertically through the opening and is hung centrally from a spider which spans the opening at the top. This shaft is eccentrically moved at the bottom and is equipped with a conical crushing head, which operates between the inclined sides of the shell. The largest of these machines with a 72-inch wide annular opening weighs about 700 tons, is driven by a 500 horsepower motor, and is capable of crushing 2,500 tons per hour to 9-inch pieces.

The minus 6-inch or 9-inch product of this machine then passes to several smaller gyratory crushers, operating on the same general principle, which produce a product 1½ to 2 inches maximum size.

Following screening on impact or vibrating double-deck screens for removal of material already reduced to wet-milling size, the oversize is passed through a tertiary stage of crushing for finer reduction using

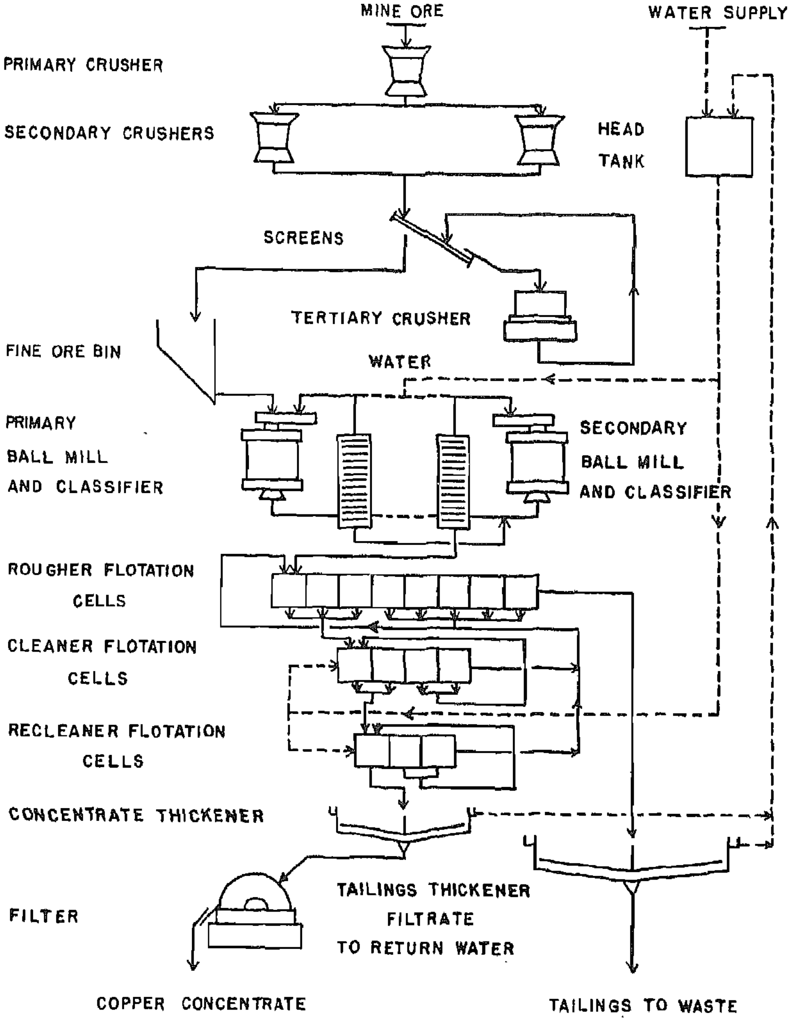

FIGURE 3-1. Simplified flowsheet of typical copper concentrator.

a higher-speed cone-type reduction machine, and the product recirculated over the screens until it is reduced to about minus 5/8 inch, though the actual size varies considerably in practice.

The tertiary crusher most commonly used for this last stage is a modification of the gyratory type. In some types the conical crushing head is eccentrically mounted on a vertical drive shaft that is supported entirely from below. The top "mantle" is spring-loaded to take care of tramp iron and over-loads, and the clearance between the crushing faces is adjustable by rotating the top assembly, which is attached by a heavy threaded connection to the frame of the machine.

Transfer of ore from one machine to the next is accomplished by a combination of gravity flow and the use of inclined belt conveyors where delivery to a point of higher elevation is required.

In general the crushing section of a typical concentrator is designed to operate 8 to 12 hours for the production of 24 hours of feed to the fine-grinding sections (say 1,000 to 2,000 tons per hour). To make this possible, ample storage of the mill feed (minus 5/8-inch material) must be provided, and it is not unusual to find a "fine ore" bin capacity of 20,000 tons or more for this purpose.

Grinding and Classification

On account of the fine dissemination of the copper minerals within the rock-forming material in the case of most of the copper occurrences in the world, the ore must usually be ground to particles passing at least a 48- or 65-mesh sieve before an economical separation can be made.

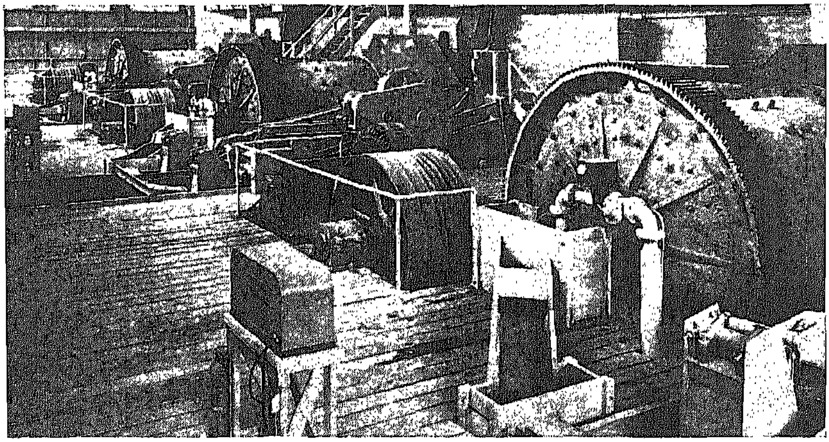

FIGURE 3-2. Grinding section of Bagdad Copper Co., Hillside, Arizona, showing ball mills in closed circuit with Dorr classifiers.

In consequence the wet grinding and classification sections of copper concentrators as compared with other sections require the most substantial equipment and are the most costly to operate—principally because of high power demand for this fine grinding.

The most commonly used grinding machines are ball mills of the cylindrical or cylindro-conical type. The cylindrical mill consists of a steel shell, ranging from 7 to 10 feet in diameter and of about equal length (in the cylindro-conical mill the length of the cylindrical portion is less than the mill diameter), lined with heavy detachable manganese steel or other wear-resisting liners and loaded with up to 45 tons of steel or iron balls of varying sizes from about 4 inches in diameter down. The mill is carried on large-diameter trunnion bearings set on concrete pedestals and is rotated within the range of 16 to 24 rpm by a 150- to 800-horsepower motor, frequently of the synchronous type. The ore, together with a sufficient quantity of water, is fed into the mill where it is crushed by the ball action and discharges from the opposite end by displacement, or by the help of a "grate" discharge provided with lifters. The principle followed in modern grinding technique is to pass the material through the mill at a high rate of flow and to separate out by means of a mechanical classifier the finished product as rapidly as it is produced, thereafter returning the oversize back to the mill feed. This increases mill efficiency and avoids the needless waste of power and other disadvantages (see Flotation) of over-grinding, arising from the old practice of trying to grind the ore to some limiting size in a single pass through the mill. Circulating loads up to three or four times the original feed are usual practice.

The mechanical classifier is a comparatively shallow steel tank 6 to 12 feet wide, having a sloping bottom 20 to 30 feet in length. It is usually installed close to, and parallel to the axis of the mill, so that the mill discharge can flow by gravity into the classifier "pool," which is kept in a state of agitation by means of reciprocating or spiral rakes. The coarser sandy portion (oversize) is conveyed up the sloping deck where it emerges from the pulp, is drained, and discharges into the scoop feed box of the same or another mill. The fines (finished fraction) overflow a weir provided along the opposite end of the machine. The largest machines are capable of handling over 12,000 tons of sand per 24 hours. Power requirements are nevertheless quite low.

In most of the larger installations, grinding and classification are carried out in at least two stages. The overflow from the primary grinding circuit discharges into the classifier of the secondary circuit, with water and other adjustments made to overflow about a minus-20 to minus-28 mesh product from the primary classifier and a final minus 48 or 65-mesh product at 18 to 25 per cent solids from the secondary machine.

Flotation

The mixture of fine solids and water, or "pulp," is next passed into the flotation machines, which consist of shallow tanks of steel or wood construction, seldom over 5 feet square and 5 feet deep, each provided with a motor-driven agitating and aerating mechanism. These individual tanks or "cells" are connected in strings of 10 to 20 units, so that the pulp entering the first cell passes successively through all the rest before discharging from the last unit.

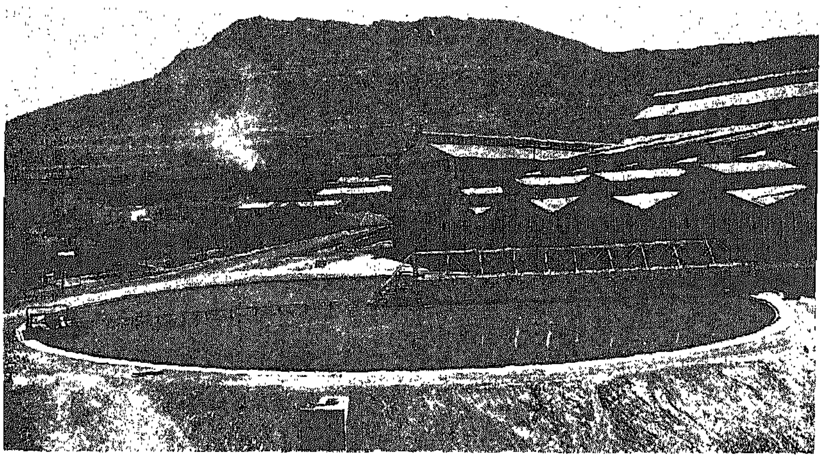

FIGURE 3-3. The Arthur mill of the Utah Copper Co. with 200-foot diameter Dorr thickener in the foreground, used for thickening ahead of flotation.

Another type of machine consists of a single, long tank or trough, in which the mechanisms or air pipes (in the pneumatic type) are spaced at regular intervals.

Overflow weirs, with or without froth raking mechanism, are arranged along one or both sides of the two types of flotation machines and adjustable weirs in the partitions between cells control the height of the pulp level.

The principle involved in ore flotation is the selective air-filming of the sulfide minerals which are subsequently floated or rafted up to the surface by a mass of rising bubbles, to be removed as a froth, while the rock-forming minerals or gangue remain in suspension, or sink for discharge from the cell at lower elevation.

The flotation process involves the continuous addition of carefully controlled amounts of at least two principal classes of chemical reagents. One of these is a frothing agent, such as pine oil or cresylic acid, which, by lowering the surface tension, assists in promoting the formation of a temporarily stable foam, or emulsion of air in water. The other is a "collecting" agent (of the heteropolar, organic type) which selectively films the copper minerals, rendering them water-repellent, attachable to the air bubbles and so rafted or floated to the surface of the pulp. The amount of frother and collector used is of the order of 0.05 and 0.25 pound, respectively, per ton of ore treated.

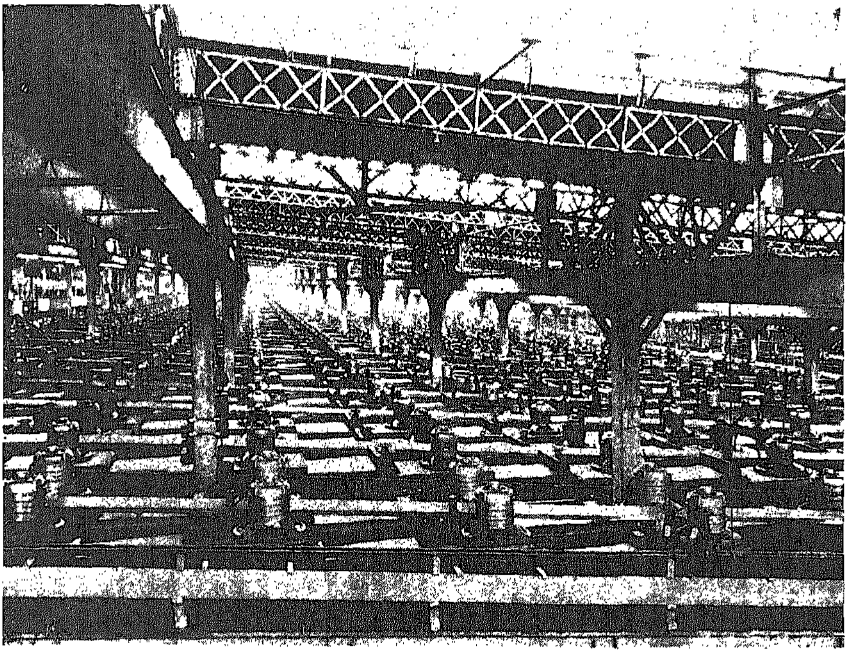

FIGURE 3-4. Interior view of the Arthur mill of the Utah Copper Co., showing flotation section.

Referring to the flowsheet (Figure 3-1) it will be noted that the mineralized froth, or "rougher" concentrate, from the first string of cells is passed to the first-stage cleaners, and the concentrate from these to the second-stage and perhaps third-stage cleaners, where the addition of water to dilute the froth permits much of the entrained waste and "middling" material to drop out and appear in the "cleaner tailing"—thereby further enriching the concentrate in copper content. These cleaner tails are then returned by pumps to the head of the rougher cells for further treatment.

Disposal of Products

The enriched concentrate from cleaner cells carrying about two parts of water to one of solids is usually dewatered in a thickener, where the solids settle into a thick sludge of 50 to 75 per cent solids, which is moved to a center cone by means of a slowly revolving submerged raking mechanism. The removal of this sludge is controlled by a diaphragm-type positive-action pump, which delivers it to one or more continuous vacuum filters, of the drum or disc type, which are built in sizes up to 500 square feet of filter-cloth area. These discharge a filter cake carrying not over 10 to 12 per cent moisture for conveying to the smelter bins or railroad cars.

The thickener overflow water and the clear filtrate are normally returned for reuse in the grinding and flotation circuits.

The tailings from the flotation plant, which may carry up to 4 or 5 tons of water per ton of solids, are almost invariably dewatered in thickeners, either of the center-drive or traction type, and may involve the use of one or more units up to 350 feet in diameter in order to obtain the required settling area.

The tailings thickener tanks are usually of concrete construction with an overflow launder around the periphery. In the traction type the raking mechanism, which is supported by a truss structure carried at one end

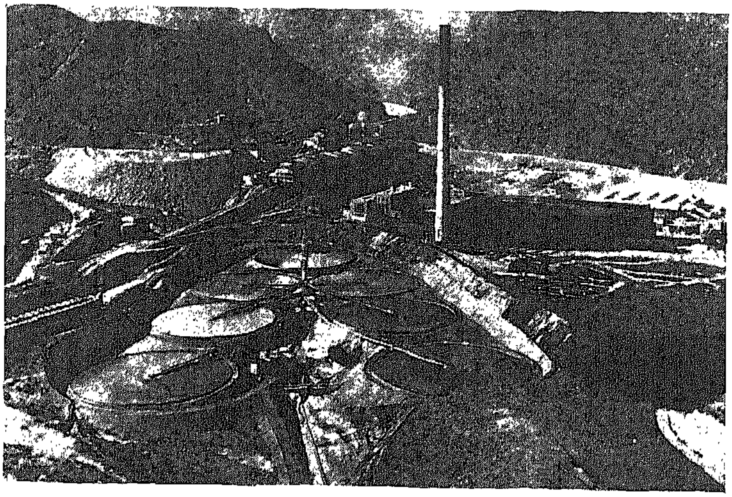

FIGURE 3-5. The Morenci, Arizona, concentrator of the Phelps Dodge Corporation, with seven large Dorr thickeners for tailings dewatering in the foreground.

on a center pier and at the other by a motor-driven traction device running on a circular rail, usually requires a half hour or more to make a single revolution. The settled solids are carried to the center by the raking mechanism, where they discharge at about 50 per cent solids and are transferred to a tailing disposal area by centrifugal pumps.

As in the case of the concentrate thickener, the tailings thickener overflow, and frequently overflow from the tailings pond, is reused in the milling circuit, which, because it consumes about one ton of water for each ton milled, is a considerable item in milling cost, particularly in arid regions.

General

Modifications in the typical flowsheet described include the use of wet rod mills or dry or wet crushing rolls handling up to 1½-inch feed in place of the tertiary crushing stage; the interposition of flotation between the primary and secondary grinding stages, with the classification, regrinding, and reflotation of the flotation tailings; the regrinding of flotation middlings and cleaner tailings in a separate circuit for the release of "locked" values before they are returned to the flotation roughers; and the regrinding and selective flotation of the final copper concentrates for the recovery of molybdenum, both products being separately thickened and filtered in conventional circuits.

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Chapter 4

Roasting, Smelting, and Converting

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Of the three main types of copper ores, native, oxide, and sulfide, the sulfide ores are most widely distributed over the continents of the world and constitute the major source of copper. When many of the metallic and oxide deposits of copper ore had been depleted or partially exhausted toward the last quarter of the nineteenth century, copper metallurgists were faced with the problem of using sulfide ores. Oxide ores and roasted sulfide ores were smelted together to produce a high-grade matte. These mattes were shipped to Wales to be treated by the Welsh process, which was essentially the interaction of copper sulfide and oxide. These are the same reactions which take place in a modern copper converter.

In 1880, Manhès developed the first copper converter by designing a vessel into which air was blown for the oxidation of the iron in the matte, thus permitting the second stage of oxidizing the sulfur in the copper. This avoided the use of the slow, laborious, and expensive Welsh process. The Manhès converter was introduced in Montana in 1885 at the Parrot Works.

Most copper ores are low grade, containing 0.8 to 2.0 per cent copper; consequently they are crushed and concentrated. The ratio of concentration varies from 2:1 (in the case of the copper-nickel ores) to 40:1 with some of the low-grade porphyries. As a rule, the ores of Africa are of higher grade, as this continent has been opened to extensive copper exploration only in recent times. These ores generally contain a mixture of chalcopyrite, chalcocite, bornite, and some oxides.

The concentrates from the porphyry ores contain from 25 to 40 per cent copper, concentrates from the primary sulfide ores contain from 5 to 25 per cent copper, and concentrates from the Central Africa ores contain up to 50 per cent copper.

Because of the difference in grade, the high-copper concentrates are generally wet-charged directly without drying or roasting, while the lower-grade concentrates as a rule are first roasted and then charged while still hot to the reverberatory furnaces.

The chief types of furnaces used now in the pyrometallurgy of copper are: (1) roasters, which are gradually losing their importance; (2) blast furnaces, which have already lost their importance; (3) electric furnaces, of growing importance especially in those countries deficient in cheap fuels and with cheap hydroelectric power; (4) reverberatory smelting furnaces, which is the type now almost universally used; (5) holding and anode furnaces; and (6) cathode refining furnaces, some of which are being replaced by continuously melting electric furnaces.

Electricity is destined to play a more important part in copper pyrometallurgy in the future as a substitute for ordinary fuel.

A condensed outline of copper ore treatment is given in Table 4-1 (due largely to Hayward).

ROASTING

The essential requirements for proper roasting are (1) chemical; (2) thermal; and (3) mechanical design.

If the charge available is not self-roasting, then extraneous heat must be added in some form of fuel, which may be natural gas, fuel oil, or pulverized coal. The best roasting temperature is a bright red heat, between 700 and 750°C (1290-1380°F). The temperature must be such that the charge does not sinter. Other things being equal, the hotter the calcines enter the reverberatory furnace, the less fuel is required in the smelting operation.

The latest type of multiple-hearth roaster is a well-designed mechanically equipped furnace. If properly run, it requires little labor, infrequent repairs, and constantly exposes fresh sulfide surfaces to oxidation; but it does make large quantities of dust. Cottrell (electrostatic) precipitation has overcome one of the greatest objections to the multiple-hearth roaster.

There are two outstanding styles of roasters, one with a conical hearth section and one with a spherical hearth section. Each type has its advantages and disadvantages. The conical hearth limits the diameter—say 21 feet 6 inches—but the hearths are closer together, thus saving head room. A spherical hearth can be of larger diameter, which in this type is limited only by the height between hearths.

For standard roasting practice the number of hearths varies from eight to twelve, depending upon the mineralogical, chemical, and physical condition of the charge.

Roasting at present involves the treatment without fusion of copper ores or concentrates, in equipment designed for the removal of part of

TABLE 4-1. TREATMENT OF COPPER ORES

Native Copper Ores		*Oxide Copper Ores*				*Sulfide Copper Ores*			
High Grade	*Low Grade*	*High Grade*		*Low Grade*		*High Grade*		*Low Grade*	
		Coarse	*Fine*†			*Coarse**	*Fine*‡		
Smelt in reverberatory furnace	Crush Concentrate Smelt in reverberatory furnace	Mix with coarse sulfide ores and smelt in blast furnace	Mix with fine sulfide ore, or concentrate and smelt in reverberatory furnace	Crush Leach		Crush Smelt in reverberatory furnace	Roast and smelt in reverberatory furnace	Crush Concentrate 10-50 per cent copper	
				Electrolyze solution to produce electrolytic copper	Precipitate with scrap iron and smelt the copper			Smelt wet concentrates in reverberatory furnace	Roast Smelt hot in reverberatory furnace

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* Coarse ores may be crushed and treated as fine ore.

† May be mixed with fine sulfide ores before roasting or added in one of lower roaster hearths.

‡ May be sintered and smelted in blast furnace.

their sulfur. The latter is reduced to the point where the ores or concentrates are ready for treatment in either reverberatory or blast furnaces. If in the latter, it will have to be sintered first. In reverberatory practice, low-grade matte is needed if slag losses are to be held at a minimum and if converters, in which the matte is subsequently treated, are to be used to the best advantage for the smelting of fluxing ores.

Coarse ores—massive sulfides—may be treated in shaft furnaces, using a large excess of air, without preliminary roasting; to all intents and purposes roasting and smelting here are combined in one operation.

The roasting of sulfide ores results essentially in the oxidation of sulfur to sulfur dioxide (SO_2). Metallic oxides also are formed; these in turn may react with SO_2 to form sulfates. Roasted ores or concentrates consist then of sulfides, oxides, sulfates, and gangue.

With the modern roasters it is possible to obtain different kinds of roasts: (1) oxidizing; (2) reducing; (3) sulfating; (4) chloridizing.

The copper concentrates produced now, with few exceptions, do not require roasting and in those cases where it is required, the oxidizing roast is used. In a considerable number of plants, the roasters are not used for roasting, but are used to dry the wet fine concentrates before smelting.

Figure 4-1 shows an improper way to build a roaster: (1) the insulation is only two inches of loose sand between the side wall and the shell; (2) the walls are built of red brick; and (3) the skewback bricks of the hearth are supported on the side wall. The loose sand will allow acid condensation and corrosion of the steel shell, the sand will leak out, and the thrust of the hearth will cause the unreinforced steel shell to bulge[1].

Figure 4-2 shows how these defects may be overcome. The insulation is designed to maintain the temperature of the steel shell at about 230°C (446°F). This is hot enough to prevent acid condensation, is a safe temperature before steel starts to lose its tensile strength, and will reduce the radiation losses and improve the working condition around the roasters. The concrete curb around the shell at floor-level prevents damage to the insulation. The side walls are built of fire-clay brick and are not used to support the skewback brick. An allowance for expansion can be left at the top of the wall, so that a change in the wall will not affect the hearth. The skewback strap is very essential as it performs several functions; it saves buying a steel shell of greater thickness, it prevents the thrust of the hearth from forcing the shell out of roundness, it increases the life of the hearth, and it prevents the hearths losing brick when for any reason the roaster is cooled.

At plants where roasters are used the dust-laden gases are generally passed through a plate or pipe Cottrell precipitator, which recovers about 95 per cent plus of the entrained dust, which is collected and charged into the reverberatory furnaces.

In one plant, the dust is collected from the Cottrells by screw conveyors into a drag conveyor which delivers it to one bin feeding a Fuller Kenyon pump, and the pump then delivers the dust to a single distribution tank, which feeds the air-slide conveyor. This distributes the dust to the middle hearth of each roaster. In this way large quantities of relatively cool dust are not charged separately into the reverberatory furnace and there is little interference with the speed of smelting.

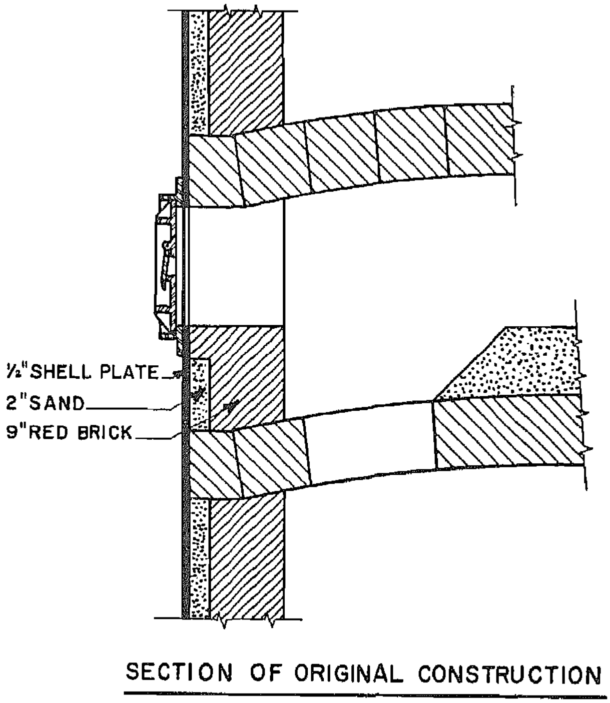
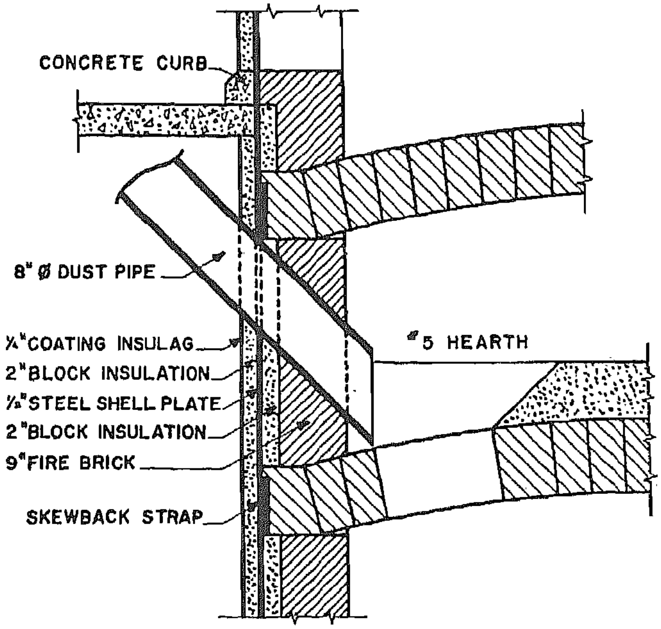


FIGURE 4-1. Sections of original construction of roaster shell and wall, showing insulation. (*Courtesy of the Canadian Institute of Mining and Metallurgy, Transactions.*)

There are two general types of center columns: (1) one made of cast sections uninsulated, and (2) one made of steel-plate sections covered with fire-clay tile. Each type has its advantages and disadvantages.

All types of columns should be reinforced at the arm so that it may break without damage to the column. Within the column should be placed the pipes to carry the cold air for cooling the arms, and the hot air may be discharged onto the bottom hearth for combustion air or wasted as operating conditions may require. By utilizing the hot air properly, it is possible to roast a charge lower in sulfur without using extraneous fuel.

If the column is made of steel plate, section brackets should be bolted to the center column at each hearth, to support properly the column tile and the metal lute rings on the odd-numbered hearth. The main weakness of the lute rings is that it is difficult to obtain bolts which connect the segments to last as long as the rings.



SECTION OF PRESENT CONSTRUCTION

FIGURE 4-2. Section of present construction, showing how defects may be overcome. (*Courtesy of the Canadian Institute of Mining and Metallurgy, Transactions.*)

The odd-numbered or "out" hearths have drop-holes around the periphery of the hearth. If these drop-holes are either too small or too large the roaster does not work properly. For a 25-foot diameter roaster, there are generally 16 drop-holes (of 2.2 sq ft) around the periphery. If the number of the holes is increased, even if each is made of less area, the roaster will run cold and require more fuel.

On the even-numbered or "in" hearths the drop-hole area is about 60 sq ft on a 25-foot diameter roaster. If the area is greater, the roaster runs cold; if less, the fines fuse on the underside of the hearth above.

A roaster designed as above, with the arms making one revolution per minute, should roast 350 tons of feed per 24 hours from 28 per cent sulfur to 13 per cent sulfur and produce a relatively hot calcine, 590-675°C (1095-1250°F), without any appreciable amount of extraneous fuel.

The amount of sulfur charged into the smelting furnace determines the grade of matte formed. Ore high in iron and sulfur may produce mattes so low in copper as to render their subsequent treatment uneconomical. The proportion of sulfur in such ores may be reduced before smelting by roasting them under oxidizing conditions. In one plant, the roasters were superimposed above the reverberatory furnaces. There are certain advantages in this, but in a warm country the working conditions would be rather severe on the personnel. In most of the plants which still use roasters, they are located away from the reverberatory furnaces and the hot calcines are trammed in specially built calcine cars.

Because of the fineness of the concentrates generally delivered for roasting, dust losses would be high were no precautions taken to prevent them; hence in most modern smelters electrostatic precipitators of the Cottrell type form an integral part of the roasting plant. Other dust-collecting devices may, of course, be installed where economic conditions do not warrant the use of electrostatic precipitators.

Chemistry of the Partial Oxidizing Roast

Since in copper metallurgy as now generally practiced only partial roasting is accomplished, the object is to oxidize some sulfur and iron and to remove volatile impurities. When the largest part of the copper mineral in a concentrate is chalcocite, little roasting is required and the roaster is used more as a dryer.

Appreciable tonnages of concentrates roasted today are a mixture of chalcopyrite, pyrite, and perhaps some pyrrhotite, together with a small amount of gangue. If the concentrates contain little silica, a siliceous ore containing copper, silver, or gold is added to the concentrates either on the top hearth of the roaster or on the belt carrying the concentrates to the roaster bin.

It is difficult to tell exactly what happens in a roaster when these three minerals are mixed together, because the proportion of each varies from time to time.

When pyrrhotite is roasted it undergoes changes as follows, according to Plattner[2]:

$$FeS + 3O \rightarrow FeO + SO_2$$
$$3FeO + O \rightarrow Fe_3O_4$$
$$SO_2 + O + \text{a catalyzer} \rightarrow SO_3$$
$$FeO + SO_3 \rightarrow FeSO_4$$

$$2FeSO_4 + heat \rightarrow Fe_2SO_6 + SO_2$$
$$Fe_2SO_6 + heat \rightarrow Fe_2O_3 + SO_3$$

According to Kothny, heating $FeSO_4$ in a current of air gives rise to the reaction $4FeSO_4 + O_2 \rightarrow 2(Fe_2O_3.2SO_3)$ within a temperature range of 150 to 380°C (300-715°F). Between 380 and 530°C (715-985°F) some SO_2 is set free; above 530°C (715°F) decomposition again sets in. The oxidation of FeS may progress more directly, as

$$4FeS + 7O_2 \rightarrow 2Fe_2O_3 + 4SO_2$$
$$FeS + 2O_2 \rightarrow FeSO_4,$$

since pyrrhotite ignites in air from 430 to 590°C (805 to 1095°F).

The formation of Fe_3O_4 (magnetite) is most undesirable, as it is reduced by FeS_2 with difficulty in a reverberatory furnace.

When chalcopyrite ($CuFeS_2$ or $Cu_2S.Fe_2S_3$) is roasted its general behavior is similar to that of pyrrhotite except that besides Fe_xO_y and $FeSO_4$, Cu_xO_y and $CuSO_4$ are formed and the formation of water-soluble $CuSO_4$ is assisted by the presence of Fe_xS.[2]

When pyrite (FeS_2) is heated with air, the elimination of S begins at 200°C (390°F). Kothny shows that 250°C (480°F) is the lowest roasting temperature. Pyrite is more readily roasted than pyrrhotite. Assuming that no sulfur is distilled, the complete oxidation of FeS_2, according to Waring, is as follows:

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

If there is a deficiency of air, Fe_3O_4 is formed:

$$FeS + 10Fe_2O_3 \rightarrow 7Fe_3O_4 + SO_2{}^*$$

According to Kothny, between 250 and 290°C (480 and 550°F) the oxidation of FeS_2 is given by

$$FeS_2 + 3O_2 \rightarrow FeSO_4 + SO_2,$$

and between 290 and 500°C (550 and 930°F) by

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

Oxidation to $FeSO_4$ takes place up to 600°C (1110°F); also

$$FeS_2 + 5Fe_2O_3 \rightarrow 11FeO + 2SO_2$$
$$FeS_2 + 16Fe_2O_3 \rightarrow 11Fe_3O_4 + 2SO_2{}^*$$

In some of the newer smelters roasters were not installed and in two new smelters, which are in the drafting stage, no roasters are contemplated. In other words, roasters are gradually being abandoned in copper pyrometallurgy. There are many reasons for this:

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* These are the reactions which produce so much magnetite (Fe_3O_4) in some calcines.

(1) Increase of dust losses due to fineness of grinding in concentrating mills.

(2) Difficulty of mechanically handling dust recovered from roaster gases.

(3) Expense of maintenance of dust-recovery apparatus.

(4) Difficulty of smelting the dust recovered.

(5) Because large tonnages of concentrates now contain sufficient copper and not too much sulfur, so that roasting performs no useful function, except to act as a dryer.

(6) If it becomes imperative to dry the wet concentrates it can be done cheaper, with the formation of less dust, by means of a special dryer than by using a roaster.

P. L. Spanne, smelter superintendent of Braden Copper Co., gives the following information concerning roasting at Caletones, Chile[3]:

"The number of roasters operating is determined by the tonnage of copper required, together with the grade of matte desired. . . . Assays on the roaster charge and roaster calcines are as follows for the year 1951 to date:

	% Cu	% S	% SiO_2	% Al_2O_3	% Fe
Roaster charge	34.9	31.8	7.2	3.4	21.3
Roaster calcines	38.4	23.6	7.7	3.9	22.9

The concentrates carry 13 to 14 per cent H_2O.

"This type of calcine, especially in a side-charged reverberatory as at Braden, has a tendency to form magnetite in the reverberatory smelting furnace. In order to help counteract this, every effort is being made to keep as much sulfur as possible in the calcines and yet get the calcines hot enough, 622 to 650°C (1150 to 1200°F), to keep them sticking to the side walls during the first part of smelting and not slide in and bridge across the reverberatory immediately on being discharged from the reverberatory fettling hoppers. These bridges, if present, will cause high bottoms which cut down furnace capacity, raise slag losses, and cause excessive fuel consumption. Two high-pressure burners are used on each roaster, the main firing being on the seventh or last hearth and the auxiliary firing on the fifth hearth as needed. Anywhere from 3 to 5 gallons of oil per ton of charge are consumed according to the varying moisture and sulfur content of the concentrates, together with the sulfur elimination desired."

A new method of roasting has been developed by the Dorr Company called "Fluosolids roasting"[4]:

"Fluosolids is the partial suspension of solid particles in an upward moving stream of gas. When so partially suspended, the solids are said to be fluidized and behave much like a liquid. The mass is boiling and bubbling, similar to boiling water. It will seek its own level, like a liquid; will overflow a weir or transfer pipe; will have an apparent density much lighter than that of the solid particles, either singly or as a settled mass. It will have a uniform consistency as to particle size, chemical composition, temperature, etc. The fluidized mass will exert hydrostatic head, and pressure taps will show differential pressure between points at various depths in the bed. The top of the fluidized mass, although irregular, like the surface of a boiling liquid, has a sharp line of demarcation from the gas above, and most important, every solid particle individually is surrounded by a film of gas or air."

It is claimed to be adaptable to roasting gold ores, pyrite, and zinc or copper ores and concentrates. Treatment of copper concentrate may be carried out either to reduce the sulfur analysis a few points, to conform to the desired matte analysis in a smelter, or it can be used to make as much as possible of the copper soluble in water and weak acid. In certain rare cases, the roasting may be for the production of strong (11-12 per cent) SO_2 gas, for acid making or other purposes.

TABLE 4-2. FLUOSOLIDS ROASTING OF A COPPER CONCENTRATE[4]

	% Cu	% Fe	% Total Sulfur	% Sulfides
Concentrates to be roasted	26.7	28.0	36.2	35.8
Calcine	22.8	22.9	9.9	0.0
Water-leach tailing	1.1	56.7		
5 per cent H_2SO_4 leach tailing	0.5	58.6		
Per cent of total water-soluble	97.7	2.0		
Per cent of total (5 per cent H_2SO_4) acid-soluble	99.0	2.6		

Table 4-2 gives the results with a 26 per cent copper concentrate.

"An important feature of the whole operation and the one where Fluosolids gives better results than obtainable with other forms of roasting is the small amount of iron that goes into solution. This is a function of temperature and atmosphere control. When these conditions are kept at their optimum, only about 2 per cent of the iron present is taken into solution."

TABLE 4-3. ROASTING PLANTS

No.	Type of Roaster	Size of Roaster	Number of Hearths	Tons of Feed per Roaster per Day	Number of Roasters	Sulfur Elimination
1.	Wedge	25′ I.D.	7	310		2 units
2.	Call and Wagstaff	19′6″ I.D.	8	250		4 units
3.	McDougall	24′ O.D. 19′6″ O.D.	5 6	200		4 units
4.	Call and Wagstaff	18′1″ I.D.	8	200		5 units
5.				173	5 to 6	33.2% to 18.4%
6.	Nichols Herreshoff	21′6″ I.D.	11	250	42	
7.	Wedge	22′6″ I.D.	8	220-250	8	31.8% to 23.6%
8.	Wedge	25′ I.D.	8	367	8 to 10	27.5% to 14.0%
9.	Nichols Herreshoff	21′6″ I.D.	11	285-370	5	29.0% to 16.0%
10.	Lurgi	21′3″ I.D.	11 7	220	4 to 8	

No.	Calcine Temperature	Fuel Used Per Ton Charge	Per Cent H_2O in Charge	Analysis of Calcines, Per Cent									
				Au	Ag, o.p.t.	Cu	Pb	Zn	SiO_2	Al_2O_3	Fe	CaO	S
1.	565°C (1050°F)	400 M. BTU	4										
2.	540°C (1000°F)	500 M. BTU	11										
3.	595°C (1100°F)	500 M. BTU	7										
4.	595°C (1100°F)	550 M. BTU	10										
5.		Pulverized coal for starting		Tr	15.0	8.8	2.8	3.6	16.6	1.5	31.1	3.2	18.4
6.	595 to 675°C (1100 to 1250°F)	43 M. BTU											
7.	620 to 650°C (1150 to 1200°F)	430 to 700 M. BTU	13-14			38.3			8.1	3.5	22.8		23.0
8.	565 to 620°C (1050 to 1150°F)	Pulverized coal for starting											
9.			13			12.5	1.1	4.3	17.3		29.7		16.0
10.	510°C (950°F)												

1. American Smelting & Refining Co., Smelter No. 1.
2. American Smelting & Refining Co., Smelter No. 2.
3. American Smelting & Refining Co., Smelter No. 3.
4. American Smelting & Refining Co., Smelter No. 4.
5. Cerro de Pasco Copper Corp., Oroya, Peru.
6. International Nickel Co., Copper Cliff, Ont., Canada.
7. Kennecott Copper Corporation, Caletones, Chile.
8. Noranda Mines, Ltd., Noranda, Quebec.
9. Hudson Bay M. & S. Co., Ltd., Flin Flon, Manitoba.
10. Bolidens Copper Co., Skelleftea, Sweden.

SMELTING

At one time metallic copper was obtained by reduction of oxide or well-roasted sulfide ores. Shaft or blast furnaces were used and carbonaceous materials employed both as fuel and for purposes of reduction, much as is coke in the iron blast furnace. The product was an impure so-called "black" copper, which contained from 85 to 95 per cent copper, and slag losses were high. Today direct reduction of copper is seldom used.

Chemistry of Smelting Sulfide Ores

The sulfide ores and concentrates are essentially combinations in varying proportions of copper and iron sulfides mixed with acid (siliceous) or basic gangue. When the charge is fed into the reverberatory smelting furnace along the side walls it forms a slope down which runs the semifused material. With the high temperature, the semifused mass is melted and forms gas, liquid slag, and matte. The material fed is a mixture of oxides, sulfides, sulfates of iron and copper, and the silicates of metals and earths. The reactions are complicated, but take place between Cu_2S and CuO; CuO and FeS; and Fe_2O_3, FeS, and SiO_2. In smelting, advantage is taken of the pronounced affinity of copper for sulfur. Of the commoner metals, copper has the greatest affinity for this element, so that when a variety of copper ores are melted together such copper as is present will invariably form cuprous sulfide (Cu_2S). If the proportion of sulfur in the melt exceeds that required to form Cu_2S, the excess will unite with any available iron (zinc, lead, etc.) to form ferrous sulfide (FeS). The two compounds Cu_2S and FeS form a series of mixtures called mattes which contain any precious metals in the original ore or concentrates. These mattes will contain anywhere from 20 to 50 per cent or more copper, and whether produced in the blast or the reverberatory furnace are "blown" in converters to obtain what is known as "blister copper." The principles underlying the "bessemerizing" of matte are simple, namely, the oxidation of iron and similar metals and the immediate slagging of the oxidized iron (FeO) with silica. When the slag is poured off, the resultant Cu_2S is blown free of sulfur, thus leaving the copper containing the precious metals.

Blast Furnaces

Blast furnaces began to lose their importance in 1916 when the flotation process for treating copper sulfide ores introduced extremely fine material which was not adapted to blast furnaces. The Dwight-Lloyd sintering machines were used in some plants to sinter a mixture of concentrates, fine ore, and blast-furnace flue dust, but even this method could only delay and not stop the gradual disappearance of the blast furnace.

There are still a few plants using blast furnaces because they are useful under particular conditions, but the quantity of copper material smelted in them produces relatively a small percentage of the world's copper.

As long as there was a large tonnage of coarse ore of high or medium grade, a blast-furnace plant was used because of a lower capital investment for each ton of ore to be smelted. As the ore (even if high-grade) became finer, it was more difficult to treat and the greater amount of flue dust (as much as 10 per cent) had to be re-treated by some auxiliary apparatus. With the reverberatory furnace the auxiliary apparatus is not required.

To run a blast furnace requires a good grade of coke, and about one and two-thirds tons of coal is required to produce one ton of coke. In 1913 when David Brown succeeded in running a reverberatory furnace with pulverized coal, the great drawback to using a coal-fired reverberatory furnace was overcome. Since a blast furnace required about 10 per cent coke and a reverberatory furnace 10 per cent coal, there was no question of the lower fuel cost to smelt a ton of ore in a reverberatory furnace. Furthermore, as much as 35 per cent of the heat in the waste gases from a reverberatory furnace can be converted into steam with a saving which is a credit to the cost of smelting in the reverberatory.

Therefore, as a result of the increasing amounts of fine material to be treated, the accomplishment of firing a reverberatory furnace with coal, later with fuel oil, and during the last twenty years with natural gas, together with the production of waste-heat steam, have made the ordinary use of the blast furnace obsolete.

As converters were made larger as a result of the introduction of basic lining in 1909, instead of the old acid lining, it was possible to convert lower-grade copper mattes. This practice made larger quantities of converter slag. The expense of chilling and resmelting the converter slag in a blast furnace is obviated in reverberatory furnace practice.

Some blast-furnace plants adopted the practice of pouring the liquid converter slag into the blast-furnace settlers and resmelting only the ladle skulls. This practice is generally thought to be neither good technique nor economical.

The chief blast-furnace plants still in operation are:

(1) Union Minière du Haut Katanga, Elisabethville, Belgian Congo.
(2) The Rio Tinto Co., Spain
(3) Mount Lyell M. & R. Co., Ltd., Tasmania
(4) The Tennessee Copper Co.

(5) Ducktown Sulphur, Copper & Iron Co.
(6) Falconbridge, Ontario, Canada
(7) Phelps Dodge Corp., Laurel Hill Plant, New York
(8) U. S. Metals Refining Co., Carteret, New Jersey
(9) International Nickel Co., Coniston, Ontario, Canada

(1). When smelting in Belgian Congo started, there were available only oxide ores; now they smelt a large percentage of sulfide ores which are sintered before smelting.

(2) (3) (4) and (5). These plants originally smelted a pyritic or semi-pyritic charge in the blast furnaces or concentrated a matte charge when acid-lined converters were used.

(6). Sinters a concentrate before smelting.

(7) and (8). Use blast furnaces for smelting large tonnages of copper scrap.

(9). Smelts a mixture of ores to make monel metal, an alloy of copper and nickel.

Since Union Minière du Haut Katanga is a large producer of copper and has always used blast furnaces for smelting, their practice will be reported in detail. The copper production is made up as follows:

Blister copper, 40 to 45 per cent
Electrolytic copper, 60 to 55 per cent

The electrolytic copper is obtained at the sulfuric acid leaching plant from oxide concentrates, mostly malachite. The blister copper is obtained at the Lubumbashi smelter, Elisabethville, by smelting copper concentrates and high-grade ore and converting the resulting matte. Oxide concentrates and ores are also smelted to obtain crude copper, which is fire-refined to anode copper used in making starting sheets for the electrolytic leaching plant.

Electric smelting is also carried out on copper-cobalt ores and concentrates for producing crude cobalt alloy which is refined overseas.

The ore from Prince Leopold mine, containing 11.5 per cent Cu and 15 per cent Zn, is concentrated by differential flotation to obtain a concentrate containing 27 to 30 per cent Cu and 12 to 13 per cent Zn, which is shipped to the smelter together with a small quantity of high-grade ore containing 25 per cent Cu and 13 per cent Zn. The zinc concentrates are shipped elsewhere.

The smelter charge is made up of copper sulfide concentrates and a small amount of high-grade ore, to which is added siliceous material of oxide ore and concentrates. This mixture, together with returned sinter, flue dust, and granulated converter slag, is sintered on Dwight-Lloyd machines. The sintered charge is smelted in the blast furnace and the resulting matte is converted to blister copper.

Below is tabulated the monthly charge to the sintering machines:

	Tons	% Cu	% Zn	% FeO	% SiO_2	% Al_2O_3	% CaO	% MgO	% S
Sulfide concentrate	23,700	28.0	12.3	19.3	7.4	1.3	2.9	2.3	24.8
High-grade ore	1,985	24.0	12.4	11.0	13.5	1.2	5.5	4.1	17.3
Copper oxides	6,280	17.9	0.6	13.1	37.6	5.1	0.8	6.5	0.6

The hourly production per sintering machine is:

Total sinter	47 tons
Net sinter for blast furnace	22 tons
Returned sinter	25 tons

The composition of the sinter is:

% Cu	% Zn	% FeO	% SiO_2	% Al_2O_3	% CaO	% MgO	% S
28.6	10.7	18.3	15.8	2.2	2.6	3.4	11.4

There are four blast furnaces measuring at the tuyère line 60 inches by 20 feet. The height from the bottom of the crucible to the feed floor is 22 feet. The furnace is charged by side-dumping cars.

The crucible of the furnace has a depth of 29 inches (between slag hole and bottom). The matte separates from the slag and collects in the crucible. The slag is tapped through a water-cooled slag breast. The matte is tapped at 10 to 12 minutes intervals through one of the two tapholes at each end of the furnace.

At present one blast furnace smelts the whole output of sinter and suffices for the blister output.

The composition of the blast-furnace charge for 24 hours is:

Sinter	1,201 tons (2,000 pounds)
High-grade sulfide ore	66
Cold converter slag	143
	1,410 tons

The coke consumption is 8.5 per cent.

Slag Analysis

% Cu	% Zn	% Pb	% FeO	% SiO_2	% CaO	% MgO	% Al_2O_3
0.9	15.7	0.6	30.3	31.1	5.0	5.8	5.2

Matte Analysis

% Cu	% Zn	% Pb	% Fe	% S	% As	Ag
64.7	5.0	2.9	5.5	21.0	0.35	32 oz. per ton

The slag is granulated and stored for future recovery of copper and zinc. The gases from the blast furnace are treated in Buell cyclones and then filtered in a bag house, the fume being collected for future treatment. The matte is tapped as required from the matte-holding furnace for the converter.

The converter silica flux is an oxide copper ore containing 4 per cent copper and 78 per cent silica. The cold "dope" is matte added while blowing to white metal and scrap copper added during the blow to blister.

The amount of matte charged per blow is 97 tons and the blister produced is 58 tons per blow, with 5.9 blows per day of 24 hrs. A little pulverized coal in a burner is used to keep the converter warm between blows.

The analysis of the converter slag is:

% Cu	% Zn	% Pb	% SiO_2	% FeO	% CaO	% MgO
13.6	14.2	7.2	20.6	29.	0.7	1.3

The analysis of the blister copper is:

% Cu	% Zn	% Pb	% Fe	% As	Ag
98.9	0.02	0.21	0.01	0.23	57 oz. per ton

The blister is shipped overseas for refining. Some blister copper is overblown in the converter and treated in the holding furnace with soda ash to decrease the arsenic content below 0.05 per cent.

The smelting operations are shut down on Sundays and advantage is taken of this to patch the tuyère line with material which is a mixture of powdered and coarse burnt magnesite with pitch and coal tar. It is shoveled cold into the converter which has been turned down with the tuyères at the lowest point. The old tuyère pipes have been pulled out and replaced by new ones with their free end closed by a welded blank.

Reverberatory Furnaces

The first recorded use of reverberatory furnaces for smelting copper ores was in 1800 at Swansea, Wales. The furnace had a hearth about 8 by 11 feet; it was built with silica or fire-clay brick and had a fused ground quartz bottom. Directly connected to the hearth was a 4-foot square firebox which was an integral part of the furnace. It was charged by hand through side doors fired by hand with semibituminous and anthracite coal in the firebox and the only draft was from the chimney. This furnace smelted 6 tons of ore per day with a fuel ratio of 1 ton of ore to 1 ton of coal. The larger furnaces today may have a hearth 111 by 33 feet; no firebox; a tamped magnesite bottom; magnesite brick side walls; magnesite brick suspended roof; may be fired with pulverized coal and smelt 2,000 tons of solid charge per day with a fuel ratio of 10 tons of charge to 1 ton of coal.

From 1800 to 1917 there was little change in the general design of reverberatory furnaces as the pattern of the Welsh furnace was copied. There was a gradual increase in the length, width, and height and toward the close of the century waste-heat boilers were added, also forced draft when found necessary.

During World War I, firing with fuel oil or pulverized coal above the hearth was gradually substituted for hand or mechanically fired furnaces. Just before the depression in 1932, in certain localities natural gas, where available and cheaper, was substituted for fuel oil or pulverized coal.

In 1917, H. H. Stout, at Douglas, Arizona, made changes in the reverberatory furnaces which had hearths 19 by 92½ feet inside. The side and end walls were made thinner so that the hearth became 22 by 94 feet. The roof was made straight without a reverb, the cross section of the combustion area increased, and the area of the uptake doubled. These changes resulted in increasing the smelting capacity by 100 per cent with a decreased fuel ratio.

Other plants gradually followed until by 1930 some plants were smelting 900 to 1,000 tons per furnace-day.

In 1935, Noranda with silica sprung arches was smelting 1,200 tons per furnace-day and the silica arches in the smelting zone were being burned out in about 80 days. Within three years, with suspended magnesite roofs, the furnaces were smelting 1,400 tons per day, and in 1941 the furnaces were widened from 30 to 35 feet and smelted 1,500 tons. By 1944, owing to shortage of labor, one furnace was shut down, but in 1945 there was too much ore for one furnace and not enough for two. Consequently, the roof on the one furnace was raised and it smelted 2,000 tons of charge per day until August, 1949, when an increased tonnage of concentrates and smelting ore was received. Again there was too much tonnage for one furnace and not enough for two. Therefore the roofs of the two furnaces were lowered to accommodate the quantity of fuel to be burned.

In Table 4-4 is tabulated information on hot-charged reverberatory furnaces fired with pulverized coal, fuel oil, and natural gas, and one heated with electricity. Table 4-5 contains similar information on wet-charged reverberatory furnaces fired with pulverized coal, fuel oil, and natural gas.

At present some plants use hot charging entirely, others use hot charging and wet charging on different furnaces in the same plant, while still others use wet charging only.

The reasons for wet charging are:

(1) When concentrates are wet and fine.
(2) When high-grade concentrates contain little sulfur and roasting would eliminate some of the sulfur required to make matte.
(3) When capital and operating expenses can be reduced by elimination of roasting.
(4) When it is possible to eliminate the large tonnage of fine roaster dust.

When doing hot charging, some plants use Wagstaff guns to spread the charge over the whole bath, instead of side charging. Each method makes considerable dust and means should be available to recover the dust, otherwise losses are high.

Unless great care is used in charging wet material, it can be dangerous. There are occasions when explosions occur, with the result that roofs have been blown off the furnaces or a firing wall destroyed. If the furnace has a deep bath of matte, it undercuts the wet material on the side walls very readily and then the material above the bath suddenly falls into the liquid matte, causing a violent explosion. Some operators corbel out the side walls, providing a base to help hold the wet charge onto the side wall.

However, wet charging does avoid roasting expense and dust losses; but it also increases the consumption of fuel. In other words, it becomes an economic question. With an abundance of cheap fuel, recovery of steam by means of waste-heat boilers, and with no cheap hydro-power, the economics could be in favor of wet charging.

In a reverberatory furnace a lower grade of matte is required than in blast-furnace practice if slag losses are to be held to a minimum and if the converters, in which the matte is subsequently treated, are to be used to the best advantage for the smelting of siliceous ores.

In blast-furnace practice, due to coke, there is a greater reducing atmosphere than in a reverberatory furnace; therefore for the same grade of matte a blast furnace makes a cleaner slag than a reverberatory furnace.

In some reverberatory furnace plants, this disadvantage is overcome by using lime to make a slag of lower specific gravity. If the lime has to be added as a barren flux, it may be uneconomical. Barren fluxes should be avoided, if possible. They may reduce the percentage of copper in the slag, but at the same time, the quantity of the slag may be increased sufficiently to offset the apparent saving.

The hot-charged copper-nickel sulfide reverberatory smelting furnace of the International Nickel Co. of Canada, Ltd., was described in the special International Nickel Co. issue of the *Canadian Mining Journal*[6]. The furnace is fired with pulverized coal. It is 110 feet long by 27 feet wide inside and the roof is made of Detrick suspended shapes of unburned chemically bonded magnesite brick. With this suspended type of roof, the furnace makes prolonged campaigns, and by adopting hot patching no major shutdowns have been necessary for repairs.

Figure 4-3 shows a plan and longitudinal section of a large hot-charged copper sulfide reverberatory smelting furnace. This furnace is 111 feet 6 inches long by 33 feet 5 inches wide inside, fired with pulverized coal, and has a Detrick suspended roof. Figure 4-4 is a cross section of the above furnace at A-A and B-B and Figure 4-5 is the cross section at C-C[1].

Figures 4-6, 4-7, 4-8, and 4-9 show plan, elevation, side wall, and cross section of a wet-charged sulfide reverberatory smelting furnace fired with natural gas and combustion air heated to 315°C (600°F)[7].

Pin-type suspended magnesite roofs, as used at the Roan Antelope plant, Northern Rhodesia[8], are an improvement over sprung arches, but are difficult to hot-patch. They are typical of Northern Rhodesia practice, where the copper in the concentrates is mostly chalcocite with some copper oxide. Consequently concentrates are high-grade and short of sulfur, so that no roasting is required. The matte made is better than 60 per cent copper and special provisions have to be used in order to convert the matte in basic-lined converters, as is described in detail under Converting.

One of the great disadvantages of operating copper mines, mills, smelters, and refineries in Central Africa is shortage of power, which at present is due to shortage of coal. Hydroelectric power is urgently needed.

From a desire to shorten the matte launders, a faulty practice has developed in some plants in handling reverberatory furnaces, namely, tapping hot matte at the firing end of the furnace, which is near the converter aisle, and skimming slag at the opposite end. The flow of the liquid material is toward the colder end (or gas-exit end) of the furnace. By this practice, there is no reservoir of matte under the slag to keep the magnetite in suspension; consequently, the magnetite crystallizes on the bottom and gradually fills up the furnace. Some operators believe that a furnace should be tapped near the skim end (preferably on both sides) into ladles on cars and the slag skimmed through the end wall.

TABLE 4-4. REVERBERATORY FURNACES (HOT CHARGED)

No.	No. of Reverberatories	Size of Reverberatory Inside	Fuel	Preheated Air	Kind of Roof	Kind of Charge	Tons of Solid Charge per Furnace-day	Btu per Ton of Solid Charge	Matte		
									Per Cent Cu	Oz. Au per Ton	Oz. Ag per Ton
1.		117'x26'6"	Natural gas		Silica arch	Hot	700-800	3,700,000	39.0		
2.		119'x25'	Natural gas		Silica arch	Hot	925-1040	3,300,000	43.5		
3.		104'x22'	Natural gas		Silica arch	Hot	700-750	3,800,000	44.0		
4.		115'x24'	Fuel oil		Silica arch	Hot	900-1000	3,500,000	39.7		
5.	2	100'x25'	Oil, coal, gas		Silica arch	Hot	650-800		19.5		32.0
6.	7 (Ni-Cu)	110'x27'	Pulverized coal	315°C (600°F)	Suspended magnesite	Hot	1200		Ni+Cu 13.0		
7.	2	122'x24' 117'x24'	Fuel oil		Slotted silica arch	Hot	1370 1235	2,750,000	50.3		
8.	2	111'6"x33'6"	Pulverized coal	180°C (360°F)	Suspended magnesite	Hot	[d]2000 [e]1400	2,553,000	22.1	0.80	6.5
9.	3	100'x28' 100'x32'	Natural gas		Silica arch	Hot	800 1000	3,800,000 3,500,000			
10.	1	100'x29' to 22'	Pulverized coal		Suspended magnesite	Hot	1600 1400	3,200,000 2,800,000	26.0		
11.	1	[f]77.1'x19.7'	(Electric power)		Fire-clay arch	Hot	540	353 K.W.H. per ton	36.2		

No.	Slag, Per Cent											Waste-heat Boilers	Steam Pressure (psi)	Method of Charging	Converter Slag Returned to Reverbs.
	Oz. Au per Ton	Oz. Ag per Ton	Cu	SiO_2	MnO FeO	CaO	Al_2O_3	MgO	S	ZnO	Pb				
1.			0.32	39.0	34.8	11.0	6.0							Wagstaff Gun	Liquid
2.			0.40	39.0	44.0	7.1	5.0							Wagstaff Gun	Liquid
3.			0.37	39.0	43.0	9.0	6.0							Wagstaff Gun	Liquid
4.			0.38	39.5	35.0	8.0	6.0							Wagstaff Gun	Liquid
5.		0.60	0.50	31.8	48.9	5.6	3.5		1.6	4.2	1.0			Side Feeding	Liquid
6.				36.0	47.6		7.0					1-1200 B.H.P. 2-1800 B.H.P. 2-750 B.H.P.		Side Feeding	Liquid
7.			0.88	27.4	54.5	0.7	11.9	0.6	1.2			No boilers		Side Feeding	Liquid
8.	0.005	0.076	0.34	38.3	46.4	1.4	6.3	1.0	1.5			1-1000 B.H.P. 3-750 B.H.P.	175	Side Feeding	Liquid
9.												2-1000 B.H.P. 1-800 B.H.P.	340	Side Feeding Wagstaff	Liquid
10.			0.42	36.2	42.7	1.7	6.2	3.5	1.0	5.7	0.3			Side Feeding	Liquid
11.	0.01	0.08	0.40	38.3	38.1	3.7	5.8	1.9	1.5	5.7	0.8	No boiler		Side Feeding	Liquid

1. American Smelting & Refining Co., Smelter No. 1.
2. American Smelting & Refining Co., Smelter No. 2.
3. American Smelting & Refining Co., Smelter No. 3.
4. American Smelting & Refining Co., Smelter No. 4.
5. Cerro de Pasco Copper Corp., Oroya, Peru.
6. International Nickel Co., Copper Cliff, Ont., Canada.
7. Kennecott Copper Corporation, Caletones, Chile.
8. Noranda Mines, Ltd., Noranda, Quebec.
9. Phelps Dodge Corp., Douglas, Arizona.
10. Hudson Bay M. & S. Co., Ltd., Flin Flon, Manitoba.
11. Bolidens Copper Co., Skelleftea, Sweden.

Note a. As shown Smelters Nos. 1 and 3 furnaces are operating substantially under capacity due to insufficient tons available.

Note b. Cost unit tons are the tons of new metal-bearing material charged plus by-products smelted less by-products produced.

Note c. All reverberatory furnaces are of similar construction, consisting of basic brick crucible with water-cooled pipe coils around feed guns. Some of furnaces have water-cooled copper jackets at bathline. The 20″ sprung silica arches are maintained with slurry coatings.

Note d. When running one furnace with roof raised.

Note e. When running two furnaces with lowered roof.

Note f. Electrode consumption per ton of total charge (excluding molten converter slag) is 2.8 lb per ton (2000 lb).

TABLE 4-5. REVERBERATORY FURNACES (WET CHARGED)

No.	No. of Reverb-eratories	Size of Reverbs. Inside	Fuel	Pre-heated Air	Kind of Roof	Kind of Charge	Tons of Solid Charge per Fur-nace-day	Btu per Ton of Solid Charge	Fuel Ratio		Matte		
									Gross	Net	Per Cent Cu	Oz. Au per Ton	Oz. Ag per Ton
1.	1	80′x20′	Oil		Silica arch	Wet	400	5,328,000	37 gal.		35 to 40		
2.	2 (Cu)	110′x24′	Pulverized coal	315°C (600°F)	Suspended magnesite	Wet	580	6,000,000			Cu 38.5 Ni 3.5		
3.	2	118′x28′8″	Natural gas	315°C (600°F)	Silica arch	Wet	815	5,620,000			39.0		
4.	2	127′8″x27′8″ 127′8″x28′8″	Pulverized coal		Silica arch	Wet	820	4,860,000	22.1%	8.6	32.8	0.32	1.65
5.	2	100′6″x28′	Pulverized coal	175°C (350°F)	Suspended roof	Wet	490	4,240,000	16%		61.3 62.1		
6.	3	95′x28′ 120′x28′	Pulverized coal	175°C (350°F)	Suspended roof	Wet	520	5,050,000	18.6%		62.7		
7.	4	88′x28′	Pulverized coal	175°C (350°F)	Suspended roof	Wet	500	5,576,000	20.5%		61.0		
8.	4	100′x30′	Natural gas		Silica arch		700 725	5,700,000 7,000,000			34.5	0.02	1.4

No.	Slag, Per Cent										Waste-heat Boilers	Steam Pressure, Psi.	Method of Charging	Converter Slag Returned to Reverberatories	Pounds of Steam per Hour
	Oz. Au per Ton	Oz. Ag per Ton	Cu	SiO_2	FeO MnO	CaO	Al_2O_3	MgO	S	Fe_3O_4					
1.			0.50	36 32	45 50	2.0					2-750 B.H.P.		Side Feeding	Liquid	
2.				36.0	50.1		5.5				No waste-heat boilers		Side Feeding	Liquid	
3.			0.57	31.3	54.0	2.1	6.9		1.8	11.0	4-1250 B.H.P.	480	Side Feeding	Liquid, Dutch oven	150,000
4.	0.002	0.018	0.49	36.0	44.5	4.5	7.5				2-1100 B.H.P. 3-780 B.H.P.	200	Side Feeding	Liquid, Some slag remelted	80,000
5.			0.62 0.48	37.7 37.9	32.2 29.3	14.6 16.8	7.3 7.6	1.8 1.8			2-1000 B.H.P.		Side Feeding	Liquid	
6.			0.79	37.1	28.7	17.6	8.7	2.0				275	Side Feeding	Liquid, Some slag remelted	
7.			0.90	38.0	33.6	7.7	5.4	5.5			8-750 B.H.P.		Side Feeding	Liquid, Some slag remelted	
8.	0.0003	0.01	0.40	36.4	45.9	5.3	7.3		1.2		8-750 B.H.P.	700	Wagstaff gun	Liquid	70,000

1. American Metal Co., Ltd., Carteret, New Jersey.
2. International Nickel Co., Copper Cliff, Ontario.
3. Kennecottt Copper Corp., Hurley, New Mexico.
4. Kennecott Copper Corp., McGill, Nevada.
5. Mufulira Copper Mines, Ltd., Mufulira, Northern Rhodesia.
6. Roan Antelope Copper Mines, Ltd., Luanshya, Northern Rhodesia.
7. Rhokana Corp., Nkana, Northern Rhodesia.
8. Phelps Dodge Corp., Morenci, Arizona.

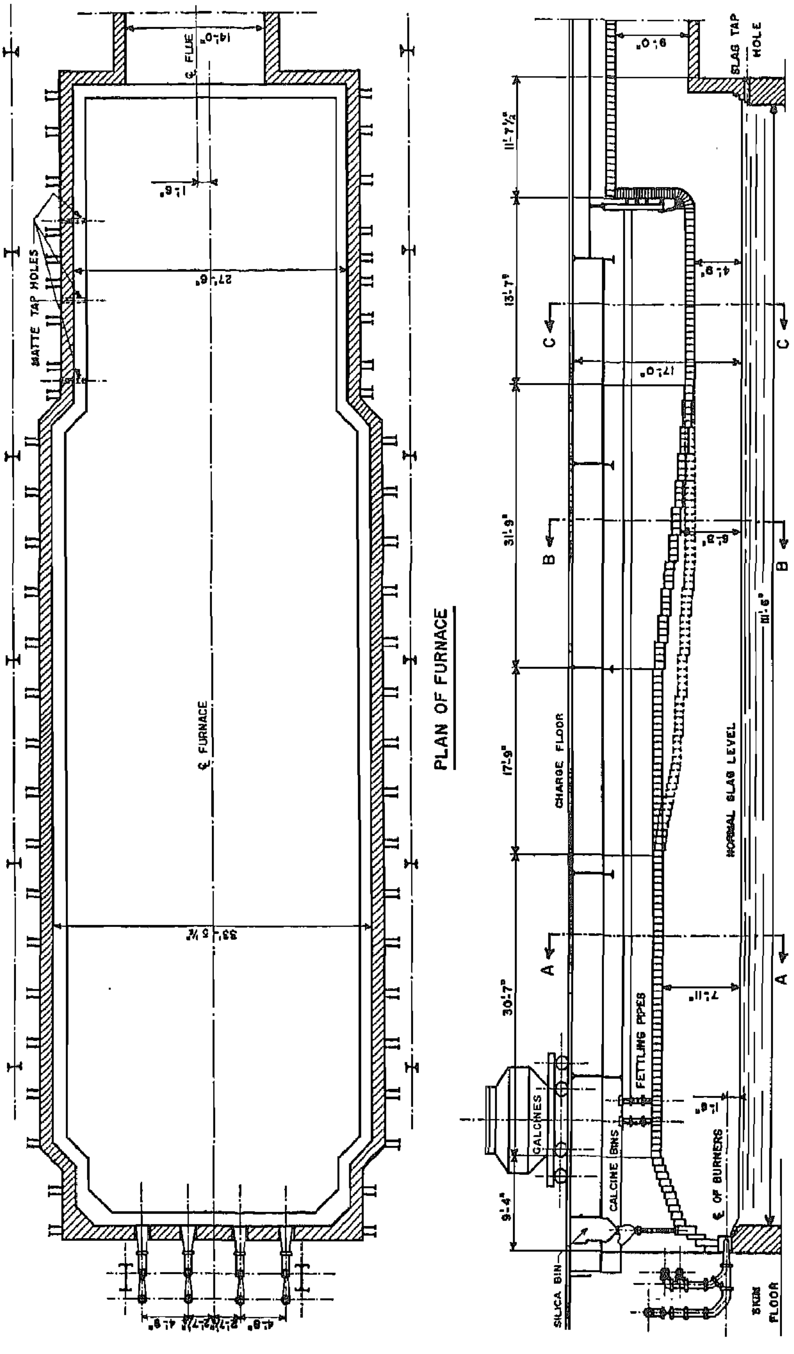


FIGURE 4-3. Plan and longitudinal section of reverberatory furnace. (*Courtesy of the Canadian Institute of Mining and Metallurgy, Transactions.*)

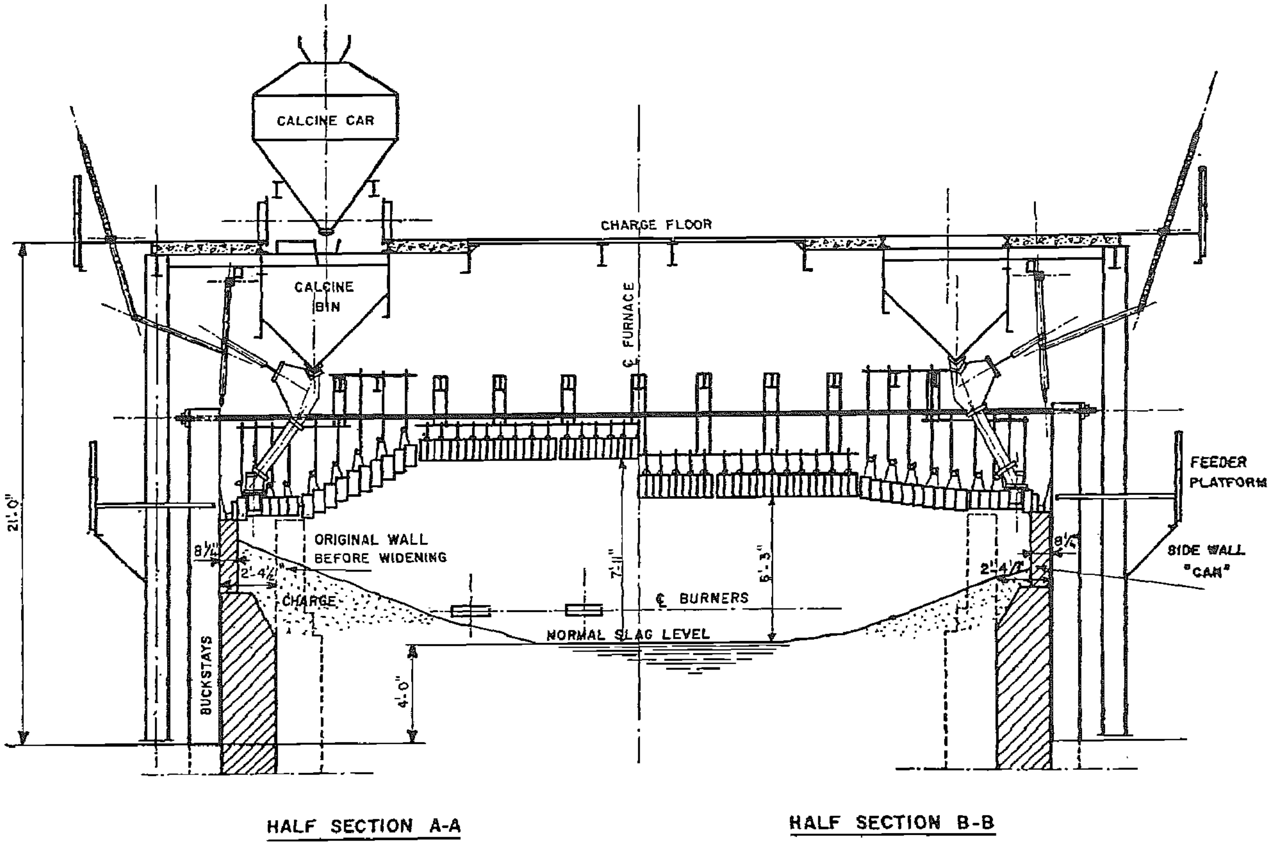


FIGURE 4-4. Half section through furnace at A-A and B-B. (*Courtesy of the Canadian Institute of Mining and Metallurgy, Transactions.*)

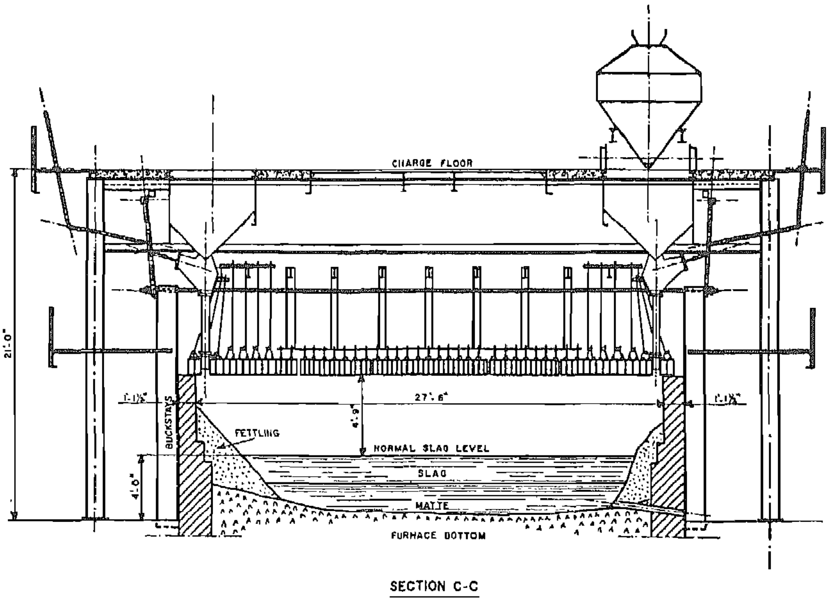


Figure 4-5. Section through furnace at C-C. (*Courtesy of the Canadian Institute of Mining and Metallurgy, Transactions.*)

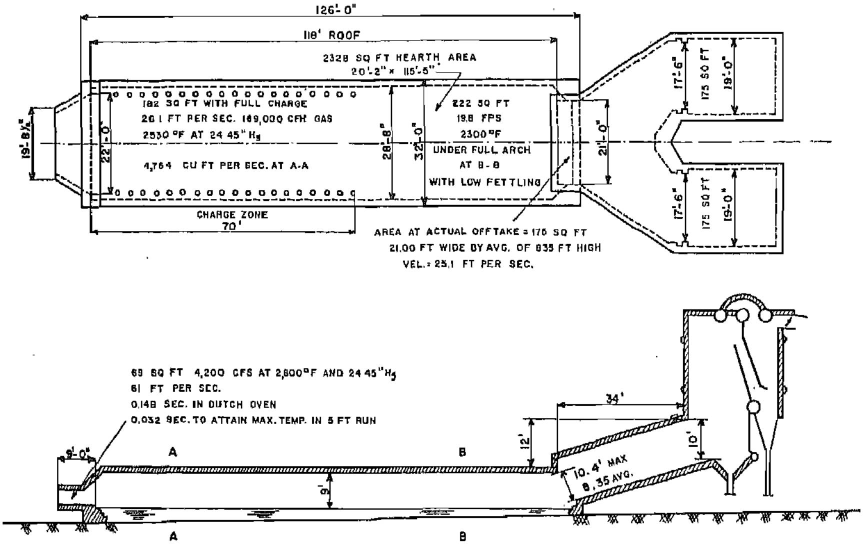


Figure 4-6. Number 1 reverberatory and Nos. 1 and 2 waste-heat boilers, Hurley plant, Chino Mines Division, Kennecott Copper Corporation. (General diagram; areas, volumes, and velocities for 169,000 cubic feet of gas per hour.)

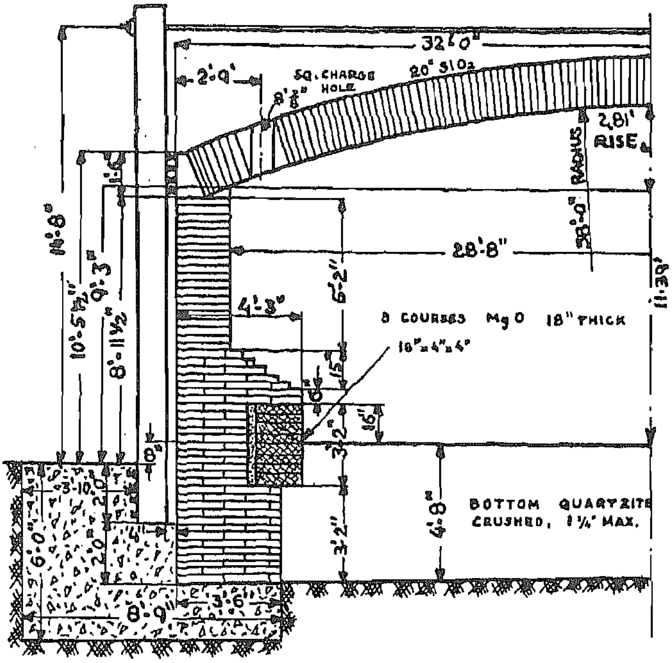


FIGURE 4-7. Number 1 reverberatory side wall, Hurley smelter, Chino Mines Division, Kennecott Copper Corporation.

One of the advantages in using reverberatory furnaces is the amount of steam recovered from the waste gases; but the ordinary power-house boiler is almost useless on such a furnace. Natural circulation on a waste-heat boiler makes a larger boiler so high that it has a stack effect on the furnace and pulls the heat out of the furnace so fast that the furnace smelts only a low tonnage but makes a large quantity of steam. Many of these difficulties have been partially overcome by a new type of waste-heat boiler with forced circulation, no baffles, and with radiation and convection chambers.

Some operators are forced to run the reverberatory furnaces to make steam. It is possible to do this making the smelting incidental, or to smelt ore with making of the steam incidental.

There is no coal in Finland, consequently, when the Outokumpu Company wanted to smelt its copper concentrates in 1936, it was necessary to design and erect an electric smelting furnace. On account of the fact that Finland in connection with the peace treaty of 1944 lost a great part of her water power to the Soviet Union, the price of electrical energy has risen so much that electric smelting is no longer economical. Con-

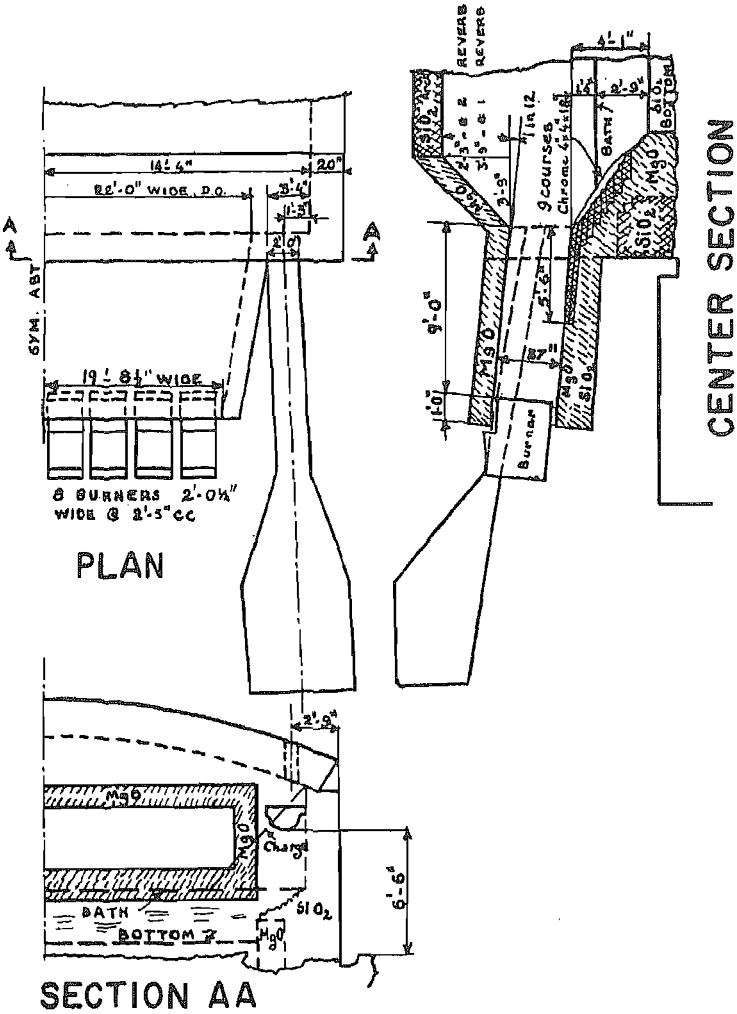


FIGURE 4-8. Burner end, No. 1 reverberatory, Hurley plant, Chino Mines Division, Kennecott Copper Corporation.

sequently, Finland has gone to the new smelting process known as "autogenous or flash smelting." Theoretical calculations show that the heat generated by burning copper concentrates containing 22 per cent copper, 36 iron, and 35 sulfur is sufficient to support a continuous smelting process, covering heat losses in the exit gases, in the smelted products of matte and slag, and through radiation. In 1946 a pilot plant was built in connection with the electric smelting furnace and was put

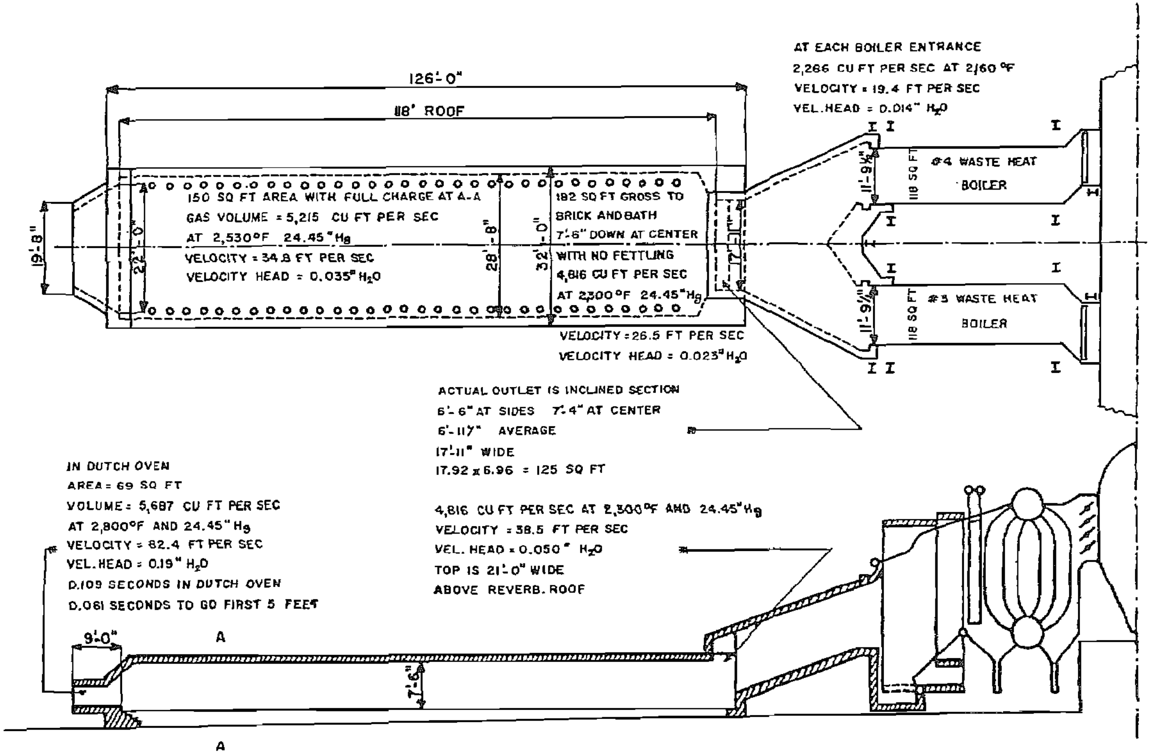

126'-0"
118' ROOF
19'-8"
150 SQ FT AREA WITH FULL CHARGE AT A-A
GAS VOLUME = 5,215 CU FT PER SEC
AT 2,530°F 24.45"Hg
VELOCITY = 34.8 FT PER SEC
VELOCITY HEAD = 0.035" H2O
22'-0"
28'-8"
32'-0"
182 SQ FT GROSS TO
BRICK AND BATH
7'-6" DOWN AT CENTER
WITH NO FETTLING
4,816 CU FT PER SEC
AT 2,300°F 24.45"Hg
VELOCITY = 26.5 FT PER SEC
VELOCITY HEAD = 0.023" H2O
17'-11"
AT EACH BOILER ENTRANCE
2,286 CU FT PER SEC AT 2,160 °F
VELOCITY = 19.4 FT PER SEC
VEL. HEAD = 0.014" H2O
11'-9¾"
118 SQ FT
#4 WASTE HEAT BOILER
#3 WASTE HEAT BOILER
ACTUAL OUTLET IS INCLINED SECTION
6'-6" AT SIDES 7'-4" AT CENTER
6'-11⅞" AVERAGE
17'-11" WIDE
17.92 x 6.96 = 125 SQ FT
IN DUTCH OVEN
AREA = 69 SQ FT
VOLUME = 5,687 CU FT PER SEC
AT 2,800°F AND 24.45" Hg
VELOCITY = 82.4 FT PER SEC
VEL. HEAD = 0.19" H2O
0.109 SECONDS IN DUTCH OVEN
0.061 SECONDS TO GO FIRST 5 FEET
4,816 CU FT PER SEC AT 2,300°F AND 24.45" Hg
VELOCITY = 38.5 FT PER SEC
VEL. HEAD = 0.050" H2O
TOP IS 21'-0" WIDE
ABOVE REVERB. ROOF
9'-0"
A
7'-6"
A

FIGURE 4-9. Number 2 reverberatory, Hurley smelter, Chino Mines Division, Kennecott Copper Corporation. Areas, gas volumes, velocities, and velocity heads. (Volumes are for 160,000 cubic feet of natural gas per hour with 7 per cent excess air.)

in operation in 1947. In 1948 a commercial size plant was erected, put into operation, and has been running since.

International Nickel has been experimenting along the same lines as the Finns except that they use enriched air, about 0.2 ton of oxygen per ton of concentrates. Although nothing has been published, it is thought that the process consists of spraying the dried concentrates into a furnace with enriched air. The smelting is said to take place almost instantaneously. The great advantages of the process are the saving in fuel and the high recovery of sulfur products. In order for such a process to show a profit, low-cost production of oxygen is required. World shortage of sulfur has added a further incentive for the process.

The Hudson Bay Mining & Smelting Co. is now recovering zinc from its reverberatory furnace slags, using a modified slag-fuming process commonly used in lead plants. Since the copper concentrates contain zinc, the copper reverberatory furnace slags also contain zinc. The slag is skimmed intermittently into an electric holding furnace and from there goes to the fuming furnace where powdered coal is blown through the slag. Although nothing has been published on the process, it is presumed that the zinc is recovered as zinc oxide. This additional process should materially increase the recoverable zinc.

Reverberatory Furnace Smelting at Phelps Dodge Corporation

A report received from C. R. Kuzell, Assistant General Manager, Phelps Dodge Corporation, Douglas, Arizona, supplies information on reverberatory smelting at the plants of that company. It is given below just as written by Mr. Kuzell[12].

The reverberatory smelting conducted at the Arizona smelters of Phelps Dodge has been for the production of copper matte from either hot calcine or cold moist concentrates. Until recent years the former was the predominant, but now the latter prevails. The information will vary in accordance with whether the charge was hot calcine or moist concentrates.

Hot-Calcine Smelting. Slag losses vary in accordance with the type of slag it is possible to make from the materials available and has some relationship to the grade of matte being produced. In general, it may be stated that the loss of copper in the slag is 1/100th of the weight of the iron in the slag; however, if the slag happens to be of inferior properties or the matte-grade higher than normal, the loss will be 1/80th. On the other hand, for exceptionally good conditions, including good workmanship, the slag loss will occasionally be less than 1/100th, even as low as 1/120th of the weight of the iron.

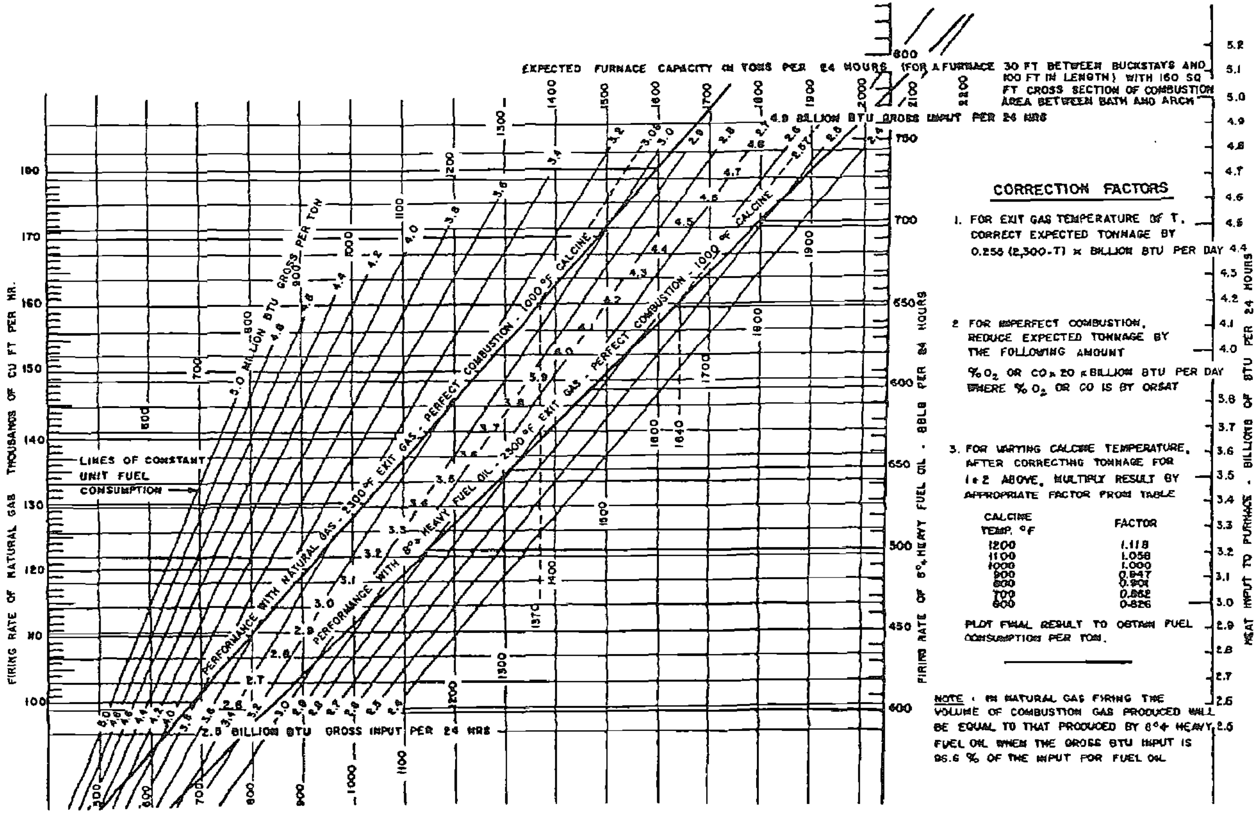
The length of the Phelps Dodge furnaces is from 100 to 110 feet inside the binding. The width varies from 30 to 34 feet inside the buckstays. All of the furnaces have sprung silica arches of about the usual radius, and the difference in elevation between the top of the bath and the highest inside point on the arch is usually around 7 feet, more or less. It is believed that the length of the furnace within the above range has no significant bearing on the smelting capacity. Some of these furnaces are arranged for bath smelting, in which case the hot calcine is fed by Wagstaff feeders. The others are arranged for side-wall smelting and are fed in the conventional manner.

It is believed that the question of tonnage and fuel ratio can only be intelligently answered if certain conditions are specified. There are so many factors governing tonnage and fuel ratio that only a complicated graph will supply the answer to a general question in this category. Such a graph is submitted in Figure 4-10. The data, as noted in the upper righthand corner of the graph, are for a furnace 100 feet long and 30 feet wide between buckstays, with a 160 square-foot cross section of combustion space between the bath and the arch. It is assumed that such a furnace would be amply equipped with sufficient gas outlet area and waste-heat boiler capacity. While the graph is more or less self-explanatory, I think it would be well to point out a few important features.

There is quite a significant loss in capacity when natural gas is used instead of fuel oil. For example, if the fuel input that the furnace plus waste-heat boilers can take is a gross input of 4.2 billion Btu per 24 hours, one finds the figure 4.2 approximately in the center of the graph along the inclined row of figures, the top one of which, namely 4.9, is marked "Billion Btu Gross Input per 24 Hours." Drawing a line horizontally through the 4.2 to the left until it intersects the heavy inclined line representing natural-gas performance, one finds that the furnace capacity should be 1,370 tons with a fuel ratio of about 3.08 million Btu per ton of charge. By proceeding horizontally to the right until it intersects the line representing the fuel-oil performance, one finds that the capacity would be 1,640 tons with a fuel consumption of about 2.57. If the graph had also been made to show the performance with pulverized coal, it would reveal that with a good grade of pulverized coal performance is somewhat better than with fuel oil. Carry the illustration further with respect to the capacity on fuel oil. It will be noted that if one could put 4.9 billion Btu through the furnace and the waste-heat boilers, the furnace capacity would be about 2,000 tons and the fuel ratio about 2.46 million Btu per ton of charge. The best that Phelps Dodge has done in such smelting was at the Clarkdale smelter, where they maintained monthly averages around 1,600 tons per day with a fuel ratio of 2.60. The furnace was of the size shown on the graph. It was quite apparent that if other factors permitted, a furnace of that size could burn enough fuel to smelt over 2,000 tons per day. This experience was from 1939 to 1941. However, the practice was limited to 1,600 tons, because to have smelted more would have required a larger furnace operating crew and an additional slag removal port and probably larger waste-heat boilers. Occasional deliberate variations slightly above the 1,600 tons, such as running a day or so at 1,800 tons, indicated that 2,000 tons or more with a fuel ratio of 2.4 or 2.45 could be attainable. The graph was prepared for the smelting of a correctly proportioned charge where the ideal relationship between free quartz, chlorite, and feldspar minerals was possible and where the calcine temperature could be maintained at 535°C (1000°F) delivered to the reverberatory furnace. Such conditions as above portrayed are not always found, and when a charge must contain unduly large amounts of feldspar and clay minerals and other departures from the ideal, the capacity of the furnace of the same size and same fuel-burning capacity might be only two-thirds or only half as much as for the ideal conditions, and all sorts of results are obtained. At the present moment at the Douglas smelter, where two furnaces are operating on hot calcine, with natural-gas fuel, the tonnage is 800 to 1,000 tons per day with fuel from 3.8 to 3.5 million Btu per ton of solid charge. One of these furnaces is the conventional side-fed type; the other is substantially the same size but is a Wagstaff gun-fed crucible-type bath-smelting furnace. The latter seems to be a little more efficient than the former. In both cases the materials available for mixing the charge do not permit the ideal charge to be made and, furthermore, the grades of materials do not permit the production of calcine at the optimum high temperature.

To sum up this section on tonnage and fuel ratio of reverberatory furnaces for the smelting of hot calcine, it might be said that in furnaces of the more or less standard size being discussed above, the capacity can range from 700 or 800 tons to 2,000 or more, depending upon the type of charge, temperature of calcine, and, for the high tonnages, the availability of sufficient waste-heat boiler capacity.

Wet-Concentrate Smelting. Phelps Dodge uses the same size furnace for the smelting of cold wet concentrates as those described above for the smelting of hot calcine. Capacity is influenced by the same factors, such as the type of fuel, the type of charge, and the available boiler capacity. Overshadowing all of such factors, however, is the fundamental one that the material is cold and contains water in a range of 6.5 to 11 per cent; therefore the range of capacity of the furnace in terms of the



CORRECTION FACTORS

1. FOR EXIT GAS TEMPERATURE OF T, CORRECT EXPECTED TONNAGE BY 0.255 (2,300-T) × BILLION BTU PER DAY

2. FOR IMPERFECT COMBUSTION, REDUCE EXPECTED TONNAGE BY THE FOLLOWING AMOUNT

% O_2 OR CO × 20 × BILLION BTU PER DAY WHERE % O_2 OR CO IS BY ORSAT

3. FOR VARYING CALCINE TEMPERATURE, AFTER CORRECTING TONNAGE FOR 1 + 2 ABOVE, MULTIPLY RESULT BY APPROPRIATE FACTOR FROM TABLE

CALCINE TEMP. °F	FACTOR
1200	1.118
1100	1.058
1000	1.000
900	0.947
800	0.904
700	0.862
600	0.826

PLOT FINAL RESULT TO OBTAIN FUEL CONSUMPTION PER TON.

NOTE: IN NATURAL GAS FIRING THE VOLUME OF COMBUSTION GAS PRODUCED WILL BE EQUAL TO THAT PRODUCED BY 8°+ HEAVY FUEL OIL WHEN THE GROSS BTU INPUT IS 95.6 % OF THE INPUT FOR FUEL OIL

FIGURE 4-10. Bath smelting of hot calcine, using as fuel El Paso natural gas or 8° + heavy fuel oil. Determination of expected furnace performance. (Calculations by C. R. Kuzell and W. J. Uren.)

dry weight of the concentrates included in the charge varies from about 500 to a little over 600 tons per 24 hours. The total charge, of course, is higher, and it might be stated that the average is between 700 and 725 tons of total charge for 24 hours with fuel consumption varying from about 5.7 to 7.0 million Btu. Thus the total charge, including fluxes and moisture, will be 750 to 800 tons for 24 hours.

The slag losses in the smelting of wet concentrates in general follow about the same rule as stated above for hot-calcine smelting.

Reverberatory Smelting at Braden Copper Co., Caletones, Chile.

The following is quoted from P. L. Spanne, smelter superintendent, Braden Copper Co.: "The two most distinctive differences between Braden reverberatory operations and those of other copper plants are (1) the use of the Engblom slotted arch in the smelting zone, and (2) the quick general repairs made after each run. The slotted arch consists of using a special brick, with a diagonal cut across one of its four corners all the way down the 20-inch length of the brick (slots are approximately 1 inch on each side), for a distance of 45 feet, beginning 10 feet from the bridge wall. This type of perforated arch construction permits a small amount of air to enter and cool the lower part of the brick in this hottest and fastest-wearing zone of the reverberatory arch. There are approximately 200 slotted openings in the roof of the furnace per lineal foot of arch. Each opening having an approximate area of 0.5 sq inch, this means that there are a total of 100 sq inches of slots per lineal foot of arch or a grand total of approximately 28 sq ft open area for the total lineal length of 40 feet of slotted arch. Although this seems diametrically opposed to the more or less general opinion that reverberatory furnaces must be as airtight as possible, nevertheless Braden experience has been that a great increase in the life of brick work has been realized without any noticeable increase in the fuel ratio.

"Furnace campaigns at the present time, when we are smelting an average of 1,370 dry short tons of concentrates per day, will average between 95,000 tons and 120,000 tons per run without any repairs except for occasional hot patching around the drop-hole area and uptake. By having the brick and other material ready for a repair, and through years of experience in this type of operation, the Braden operators are able to effect an average 50-foot arch repair in less than 24 hours actual time between the time the fire is taken off and when it is put back on. In addition, by making these quick repairs the furnace is kept hot enough so that it is very seldom that the actual smelting time lost is over 40 hours except for exceptionally large repairs. This in part is explained by the fact that the slotted arch permits heating the furnace up very quickly without any spalling of arch brick."

Smelting in Electric Furnaces

Bolidens Copper Co., Sweden. This company erected and put into operation in 1949 an electric furnace similar to a reverberatory furnace 77 feet long by 20 feet wide with six continuously fed Söderberg electrodes which are placed through the roof along the center line. Each electrode is 3.9 feet in diameter. The furnace energy is 12,000 kva. The bottom is built on cast-iron plates supported by concrete pillars and the side walls up to the normal slag line are enclosed by conker plates. The furnace bottom and side walls below the slag line are made of burned magnesite brick while the side walls above the slag line consist of fire-clay and insulating bricks. The roof of the sprung-arch type is made of fire-clay brick and is insulated. The height between the deepest point of the bottom (of inverted arch type) up to the highest point of the roof inside is 9.2 feet.

The material to be charged, consisting of calcines from the roasters, flux, cold returned material from the converters, dried ore and concentrates, etc., is fed to the furnace through the roof by means of charge pipes which go up to the charge floor above the furnace. There are no bins for the charge. Even fairly great variations in the charge supply do not affect the operating conditions, due to the flexibility of the furnace operation and the ample space in the furnace both above the slag line for solid material and for liquid matte and slag. The liquid converter slag is poured into the furnace by means of a launder which enters the furnace through the roof. There are no water or air cooling devices on this furnace except at the slag and matte tapping holes.

The average tonnage smelted per day was 540 tons and the furnace ran 363 days out of 365. Two days were holidays when advantage was taken of the shut-down to replace the bricks around the matte tap-holes. The furnace is now on its third year of operation without any major repairs or shut-down. If more material were available, it would be possible to smelt an average of 900 tons of charge per day, which has been done in actual tests.

Since heat losses from the furnace are constant whether it is operating at low or high capacity, the power consumption, calculated in kilowatt-hours per ton of material smelted, will decrease at increased capacity.

The production was 28,660 tons of copper for the year 1950.

There is an outstanding advantage of an electric furnace of this type over a reverberatory furnace fired with pulverized coal, oil, or natural gas, namely, the ability to reduce easily the magnetite in such material as hot and cold converter slags and returned secondary materials. Some plants have materials which contain from 20 to 50 per cent magnetite.

In many plants the depth of matte in the reverberatory furnace is measured by means of a steel bar lowered through a hole in the roof. When this bar is withdrawn, it shows three classes of material: at the bottom, matte; in the middle, a mush (magnetite); and at the top, slag. When the depth of the magnetite exceeds a predetermined thickness, some method must be adopted to reduce it. In an electric furnace, when the measuring bar shows an appreciable depth of Fe_3O_4, the electrodes are lowered. This raises the temperature of the mush and at the same time fine pyrite and siliceous material is added to the charge. In a short time the magnetite is reduced to FeO and is combined in the slag, and any enclosed copper matte with precious metals settles with the matte. When the magnetite has disappeared, the electrodes are raised to their regular running position and the operation is repeated whenever the magnetite accumulates again. Other advantages are that an electric furnace makes little dust, whether using hot or cold charge, thus avoiding the necessity of extensive flue and dust-recovery apparatus, and the plant is always clean as there is little excuse for a large accumulation of high-grade secondaries containing magnetite. No waste-heat steam can be recovered because of the low temperature of the exit gas.

Wherever there is low-cost power available, *i.e.*, from 0.2 to 0.4 cent per kilowatt-hour, electric furnaces should be considered, especially if the amount of concentrates to be treated is small.

Union Minière du Haut Katanga[5]. Copper-cobalt ore and concentrates are smelted in open-top electric furnaces. Until recently these were all single-phase 700-kw furnaces, having one top electrode of prebaked carbon or of rammed electrode paste of 20 inches (500 mm) diameter. The bottom electrode is of rammed carbon paste. The furnaces are circular. The rim is lined with rammed carbon in its lower part and with firebrick in its upper part.

A part of these furnaces are being combined by threes into three-phase furnaces, also with a carbon bottom and with an open top. They have, of course, three top electrodes.

The metal is tapped from a hole level with the bottom. The slag is run nearly continuously from a water-cooled slag-notch which is 20 inches (500 mm) higher than the metal taphole.

These furnaces are shaft smelting furnaces. They require the feed to be substantially free from fines and to have only a moderate proportion of ore with a high fire loss. This is required to avoid explosions in the charge column.

The fine ore and concentrates are prepared by sintering on 42-inch by 33-foot Dwight-Lloyd machines. All the ores and concentrates smelted have the cobalt and the copper as oxide compounds.

The charge for the sintering plant is made up of copper-cobalt concentrates, copper-cobalt fine ores, fine sinter returned to the charge, and coke at about 260 pounds per ton of ores and concentrates.

The sinter contains 10 to 11 per cent copper and 7 to 8 per cent cobalt. It is charged into the electric smelting furnace with coarse ore, cobalt-bearing refinery slag, lime as flux, and coke for conduction of the electric current and as reducing agent. The composition of the monthly charge of the electric smelting furnaces is as follows:

	Tons (2,000 pounds)
Sinter	3,305
Coarse ore (12% Cu, 8% Co)	165
Cobalt-bearing refinery slag	275
Lime	2,315
Lump coke	155

The following slag is obtained from the smelting:

% Cu	% Co	% SiO_2	% Al_2O_3	% FeO	% CaO	% MgO
0.3	0.4	40.0	9.0	2.0	39.0	7.0

The metals which have been reduced from the charge settle in the hearth. They are tapped at intervals into a ladle where through some cooling they separate into two layers comprising alloys of different densities. The compositions of these are:

	% Cu	% Co	% Fe	% Si
Upper layer (white alloy)	15.5	47.0	31.0	1.9
Lower layer (red alloy)	85.0	7.0	4.0	0.8

The power consumption in the furnace is 487 to 510 kw-hr per ton (2,000 pounds) of charge. The consumption of rammed electrode is 5.2 pounds per ton.

The white alloy is shipped overseas for refining into cobalt.

The red alloy is refined by oxidation in a rotary furnace, and the following products are obtained:

Copper of 99.1 per cent Cu, used for making anodes for the starting-sheet section of the electrolytic leaching plant.

Slag containing 21.5 per cent Cu, 20.5 per cent Co. This slag is charged cold to the electric smelting furnace with cobalt sinter and ores.

CONVERTING

One of the outstanding achievements in copper pyrometallurgy during the last century was the successful introduction of the Manhès converter. Up until that time whenever sulfide ores were treated, the ores were roasted and mixed with oxide ores or smelted and resmelted until the matte was increased to 60 to 70 per cent copper. This grade of matte was treated in a reverberatory furnace by the Welsh process, which depended upon the interaction of Cu_2O and Cu_2S and was slow, laborious, and expensive.

The patent rights to the Manhès copper converter were bought by the Parrot smelter in Butte, Montana, in 1884, and over the years the converters have been enlarged gradually. Up until 1909, the converters were lined with siliceous material, but at that time Peirce and Smith obtained their patent on basic lining. Later Garr patented the idea of blowing siliceous material into a basic-lined converter and in 1913 Wheeler and Krejci patented the magnetite coating on the brick lining.

Although the basic lining solved many problems, it added some new ones. It was a great improvement over any other kind of converter lining. The basic lining made it possible to convert any grade of copper matte to copper in a relative short time with infrequent repairs.

The coating of magnetite on the basic brick prolonged the life of the lining, but it has to be replaced from time to time as it wears off. If it is done too often it increases the amount of magnetite in the converter slag, which thus increases the magnetite in the reverberatory furnace. In converting high-grade matte—60 per cent or more copper—there is no advantage in coating the basic lining with magnetite as it just increases this material in the furnace.

At first it was thought that fire-clay brick or insulating brick should be placed between the steel shell and the basic lining of magnesite brick, but this is not necessary and, moreover, it overheats the lining, thus shortening its life.

One of the new problems produced by the basic-lined converter, if conditions are not correct, is the large amount of magnetite made when iron sulfide in the matte is oxidized. In order to preserve the magnesite brick lining, the operators were cautioned to keep the temperature in the converter as low as possible. This is the ideal way to make quantities of magnetite. Magnetite can be reduced in the presence of an excess of FeS and at high temperatures in the presence of properly crushed siliceous material. Under these conditions the nascent iron oxide (FeO) unites with the SiO_2 to form an iron silicate slag.

Since the reactions in a copper converter should be exothermic, anything done to prevent or retard such reactions increases the chance of making magnetite.

The amount of magnetite made in a converter may be caused by one or more of the following:

(1) Too low silica content in the converter flux.

(2) Blowing the converter at too low a temperature in order to preserve the brick lining or for other reasons.

(3) Coating the brick too frequently with magnetite by blowing matte without siliceous material.

(4) Blowing a matte too high in copper, which does not allow sufficient time to develop enough heat to make slag, or in other words to oxidize the iron and flux the oxidized iron with silica.

(5) Overloading the converter with too much matte at one time.

(6) Not using closely sized flux, since miscellaneous sized flux retards the formation of the slag.

It is difficult to maintain correct working conditions within a basic-lined converter as the temperature range is small, about 130°C (235°F). It varies from 1220 to 1350°C (2230 to 2460°F). Below 1220°C (2230°F) the temperature is too low to form a true slag, while above 1350°C (2460°F) the heat will wear out the basic lining very rapidly. The slag made at 1220°C (2230°F) is a sub-silicate of the type $3FeO.SiO_2$ (containing 21.7 per cent SiO_2). As few high-grade mattes are as hot as 1220°C (2230°F) when charged into a converter[9], some heat has to be added or developed in the converter to produce the required increase in temperature. If extraneous heat is not added, then it will be obtained at first chiefly by the oxidation of iron sulfide to Fe_3O_4, which is an exothermic reaction[10]:

$$3FeS + 5O_2 \rightarrow Fe_3O_4 + 3SO_2$$

To prevent this reaction some smelters converting high-grade matte use pulverized coal or fuel oil to preheat the converter and charge until the converter is skimmed. This is the common practice in Northern Rhodesia and the Belgian Congo. When the necessary temperature has been attained to form a true slag, then the oxidation of the iron sulfide to ferrous oxide only (to unite with silica) provides ample heat, but considerably less than when magnetite is formed[10].

$$2FeS + 3O_2 \rightarrow FeO + 2SO_2 \text{ (exothermic)}$$

$$2FeO + SiO_2 \rightarrow 2FeO.SiO_2 \text{ (exothermic)}$$

or

$$3FeO + SiO_2 \rightarrow 3FeO.SiO_2 \text{ (exothermic)}$$

The two final reactions in converting are[10]:

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2 \text{ (exothermic)}$$
$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2 \text{ (endothermic)}$$

These reactions must proceed simultaneously until the end. The two above equations combined are equivalent to:

$$Cu_2S + O_2 \rightarrow 2Cu + SO_2 \text{ (exothermic)}$$

The temperature of the copper at the end is about 1030°C (1885°F), and in blowing high-grade matte there is little heat left in the copper with which to melt copper scrap. It can thus be seen that all the necessary heat to carry on the process is made by the oxidation of the iron sulfide, consequently, the matte must be at the proper temperature when starting to blow.

If the converter is not preheated, and the matte is not at the temperature of 1220°C (2230°F) when charged to the converter, it is unavoidable that magnetite will be formed at the beginning of the blow and cannot be reduced again until the temperature is above 1220°C (2230°F)[11].

$$3Fe_3O_4 + FeS \rightarrow 10FeO + SO_2 \text{ (endothermic)}$$

Copper oxide is reduced by

$$Cu_2O + FeS \rightarrow Cu_2S + FeO \text{ (exothermic)}$$

Some of these difficulties with the basic brick lined converter can be minimized by:

(1) Making the lowest grade of matte consistent with proper operation of the reverberatory furnace, thus allowing time to develop sufficient heat in the converter to make the proper slag.

(2) Making higher-silica slags (26 to 30 per cent SiO_2).

(3) Using converter flux containing from 65 to 70 per cent SiO_2 with low-grade mattes, and from 70 to 80 per cent SiO_2 for high-grade mattes.

(4) Running the converter as hot as possible without excessive deterioration of the brick lining.

(5) Using properly sized flux by screening out the plus ½-inch and the minus ⅛-inch material and by using the proper amount fed at a uniform rate.

Since it costs little to smelt siliceous ores in the converter, as no fuel and little labor are used, it is the most economical way to introduce silica into a smelting system where there is an excess of iron. As most copper sulfide concentrates today are principally composed of copper, iron, and sulfur and little silica, large amounts of silica flux are required. All that can be used in the converters avoids the roasting and reverberatory costs and losses. Whenever possible siliceous metal-bearing ores are used. There are a few concentrating mills which produce concentrates high in silica. In these cases, large quantities of silica are not required. Many operators object to increasing the silica in the converter slag or running the converters hotter as the magnetite coating (when used) wears off faster. There is, however, a nice balance that can be maintained by good operators.

Since the patents of Wheeler and Krecji (1913) were granted for the formation of magnetite coatings on converter brick linings, there have been few outstanding improvements in converter practice other than the silica gun patented by Garr. This was the idea of blowing crushed siliceous flux through a hole in the converter shell and lining during the slagging period. Experiments have been underway for many years in efforts to design a mechanical means for "punching" converter tuyères. One particular design is very promising and soon the unpleasant job of hand punching may be replaced by mechanical punchers.

Converter slags are generally disposed of by pouring them back into the reverberatory furnaces. If high in magnetite, some of this settles to the bottom and may build up the matte-holding space until the furnace has to be shut down and dug out. The magnetite which flows out in the furnace slag will increase the slag losses of metals. The matte and slag skulls as well as other converter secondaries are dumped into the converter where they are melted, or are crushed, added to the charge, and smelted. Some operators cast their converter slag, mix it with coal and pyrite, smelt the mixture in the reverberatory furnace, and thus eliminate the Fe_3O_4. Some plants may have as much as 50 per cent Fe_3O_4 in their converter slags, particularly where 60 per cent copper mattes are being converted. Everything possible should be done to reduce the magnetite formed in converter slags. Many converter slags made are low in SiO_2 (18 to 22 per cent) and therefore are high in iron, as little Al_2O_3, CaO, etc., are generally present. High-iron slags are also high in Fe_3O_4. Therefore, by keeping the silica higher the iron will be lower and less magnetite will be present.

When blowing a converter, flux should be used in the proper amounts and added slowly. If added too rapidly or in too large batches iron is not oxidized rapidly enough to form slag, thus silica mush and floaters form; and if the flux is added too slowly, the formation of magnetite is aided. In either case more matte and flux will have to be added and the converter run hotter to make a good slag.

The matte left in the converter at the end of the slagging period should be Cu_2S, called "white metal," and should be free of iron. If there is insufficient white metal left after skimming off the slag, which is usually poured hot into the reverberatory furnace, then more matte is added and the slagging period repeated until there is sufficient white metal to blow the Cu_2S to Cu without freezing. If any iron is left in the matte and any quantity of slag in the converter, there will be complications. This is a point in the process where it is possible to distinguish between a good and a poor operator. If during the copper-blowing period, the charge becomes too hot, high-grade scrap is added from time to time to keep the temperature below the point where the magnesite brick lining is injured.

One plant has recently installed constant weight feeders to supply flux to the Garr guns. These, coupled with recording and indicating air-flow meters and integrating blowing-time meters, have improved the converter practice in producing regularity in the slags and obtaining a high percentage of blowing time.

The gases from the converters contain a considerable amount of dust and are treated usually by electrostatic precipitators. The coarse dusts are returned to the converters for treatment, while the fume and finer sizes are charged directly into the reverberatory furnaces. When the copper contains low values in the precious metals, multiclones or cyclones are used instead of electrostatic precipitators.

Several companies in Northern Rhodesia and one in the Belgian Congo have developed very successful techniques in converting copper matte containing more than 60 per cent copper. In the Belgian Congo with only one converter, as much as 9,500 tons of copper per month has been made during those months when the brick lining is not repaired.

Another plant in Northern Rhodesia blowing high-grade matte claims that if cold copper or any other kind of cold material is added before copper shows on the punch rod, then little arsenic and bismuth will be eliminated.

TABLE 4-6. ELIMINATION OF BISMUTH AND ARSENIC

	1947-1948		1948-1949	
	Bi	As	Bi	As
Per cent removal in reverberatories	38.5	10.2	40.2	22.6
Per cent removal in converters	95.7	82.3	95.3	79.9
Per cent removal over-all	97.3	84.2	97.4	84.4

These are remarkable eliminations of these elements. The analysis of the blister at the same time was:

Copper	99.6 per cent
Bismuth	0.0015 per cent
Arsenic	0.0012 per cent

Another plant in Northern Rhodesia gives the following information on bismuth[8]:

"Bismuth removal in converting increases with rise in temperature of the bath, especially during fluxing, when over 50 per cent of the total bismuth removal is achieved. The temperature rises during this period to over 1320°C (2410°F). Scrap copper cannot be added after the final skim; apart from the fact that this would chill the bath, it has been found that bismuth is extremely soluble in metallic copper, and once dissolved cannot be removed thereafter by blowing. Copper scrap is added 20 to 30 minutes before the end of the blow; after this stage no further removal of bismuth takes place. No plant reverts, including matte ladle skulls, can be smelted in the converters."

When the smelter is located at a great distance from a refinery and the blister copper has to be transferred in transit, it is shipped in the form of a cake weighing about 400 pounds. However, if the blister does not have to be handled in transit, it is cast in larger cakes, or at some plants directly into anode shapes.

There are two types of converters still in use, the upright or Great Falls type, generally 12 feet in diameter and 16 feet high, and the horizontal or Peirce-Smith type, generally 13 feet in diameter and 30 feet long. Each type has its good points, but the horizontal is almost universally used.

Holding Furnaces

Holding furnaces are cylindrical shells, rotating around their long axis, and similar to a horizontal converter except that they have no tuyères but do have small openings in the ends, one for skimming slag and one for fuel, together with an additional opening through which the liquid blister copper is poured. They are lined with burned basic brick and fired with gas, fuel oil, or pulverized coal, and may be used to cast either blister cake or anodes. One plant uses a hot-metal car, fired with fuel oil, similar to a hot-metal car used in the steel industry. This car transports the liquid blister copper from the converters to the anode furnaces, situated a mile and a half distant. The car is hauled by standard railroad locomotive immediately after it is filled, and its contents poured into the anode furnace.

REFRACTORIES

Roasters are still lined or built of fire-clay brick as formerly, because it is relatively low-temperature work and because the clay brick has a low coefficient of expansion.

Copper reverberatory smelting furnaces are built principally of silica brick, with side walls made of magnesite brick below the slag line, silica

TABLE 4-7. CONVERTERS

Company	Location of plant	No. of Converters	Size of Converter	No. of Tuyères	Diam. of Tuyères	Converter Slag, (%)								
						Cu	SiO$_2$	FeO	Al$_2$O$_3$	CaO	MgO	ZnO	Pb	S
American Metal Co.	Carteret, New Jersey	1 1	13'x30' 10'x17'		1½"									
International Nickel Co.	Copper Cliff, Ontario	Ni + Cu, 15	13'x35'	13-48 2-59	2"		26.5							
International Nickel Co.	Copper Cliff, Ontario	Cu 5	13'x35'	59	2"		26.0							
Cerro de Pasco Copper Corp.	Oroya, Peru	5 1	12'x20' 13'x30'		1½"	2.05	17.3	50.9	1.2	0.7		3.5	1.8	1.6
Kennecott Corp.	Hurley, N. M.	3	13'x30'			3.9	21.4	63.2	4.2	0.6				1.2
Kennecott Corp.	McGill, Nev.	2 1	12'x30' 13'x30'											
Kennecott Corp.	Caletones, Chile	4	13'x30'			3.3	23.8	61.5						
Phelps Dodge Corp.	Morenci, Arizona	6	13'x30'			2.9	25.1	46.7	4.9	0.8				1.6
Hudson Bay M. & S. Co.	Flin Flon, Manitoba	3	13'x30'			2.0	28.0	52.7						
Bolidens Copper Co.	Skellftea, Sweden	2	13'x30'		1½"									
Mufulira Copper Co.	Mufulira, Northern Rhodesia	3	13'x30'		1½"	6.2	23.5	52.3	5.4	6.9	1.5			1.8
Roan Antelope Copper Mines, Ltd.	Luanshya, Northern Rhodesia	4	12'x20'	30	1½"	7.7	25.4	41.0	7.0	11.1	1.2			1.4
Rhokana Copper Co.	Nkana, Northern Rhodesia	4	13'x30'		2" 1½"	4.8	20.7	51.0	1.8	1.1				1.5
Noranda Mines, Ltd.	Noranda, Quebec	5	1 13'x28' 2 12'x30' 2 13'x30'	48 44 46	1¾"		27.2							
Union Minière du Haut Katanga	Elisabethville, Belgian Congo	1	13'x30'	52	2"	13.6	20.6	29.0		0.7	1.3	17.7	7.2	

brick above, and silica-brick uptakes. Roofs are of silica brick in the form of a sprung arch. Some smelters use magnesite brick in the side walls and suspended magnesite brick in the roofs. A test was run in recent years on a gas-fired smelting furnace with silica sprung arch for the roof by raising the flame temperature from 1455 to 1595°C (2650 to 2900°F); the silica brick in the side walls and the sprung arch deteriorated rapidly.

Within the last ten years C. R. Kuzell has developed the technique of blowing, by means of an air gun, a siliceous aluminous slurry on the hot undersurface of silica sprung arches and on the hot inside surface of the silica side walls. This practice has prolonged the life of the silica brick.

In Canada, about 1932-1933, John Ambrose at Flin Flon, Manitoba, installed a magnesite suspended roof on the reverberatory furnace in the hottest part of the fusion zone. Over a period of time this was extended the full length of the furnace and proved very successful, although he did no hot patching. In 1935, Noranda followed the Flin Flon practice and in the succeeding years developed the technique of hot-patching the roof while the furnace was under full fire. The method was feasible due to the existing furnace and building construction. Furnace roof campaigns are now of indefinite duration. Because of the flat angle of repose of the furnace charge the upper parts of the side walls were rapidly destroyed. This difficulty was overcome by suspending large cans filled with a magnesite mixture from the crushed furnace magnesite cobbing. These side-wall cans can be replaced like the roof brick with no interruption of full furnace operation. All Canadian copper and copper-nickel plants are using suspended magnesite brick arches. Canadian plants have practically abandoned the use of anything but magnesite brick in the construction of their furnaces. The best results are being obtained from unburned grain-sized chemically bonded and hydraulically pressed brick made of a mixture of magnesite and chrome. For roof construction brick 12 inches long are mostly used with a few 9- and 18-inch brick for patching. Present practice employs brick 3½ to 4½ inches in cross section.

FUELS

Fuel oil was first used on copper reverberatory smelting furnaces in 1906 at Humbolt, Arizona, and in 1911-1912 in Cananea, Mexico; pulverized coal in 1913 at Copper Cliff, Ontario, Canada; and natural gas about 1927 at El Paso, Texas. On the eastern and western coasts of the United States in the copper smelters and refineries, fuel oil is used almost exclusively because it can be hauled cheaply by tankers to the seaports. Some plants on the eastern seaboard are equipped to use either fuel oil or pulverized coal, whichever is cheaper. In the southwestern states and in Montana natural gas is used more frequently because it can be pumped considerable distances through pipelines. In other words the plant uses the cheapest fuel available.

Generally, the maximum flame temperature used in a reverberatory furnace with natural gas is 1400 to 1455°C (2550 to 2650°F).

In a hot-charged copper reverberatory smelting furnace, there are used 3,000,000 Btu to smelt one ton of charge irrespective of the kind of fuel used, and about 35 per cent of the heat is recovered by making waste-heat steam.

A wet-charged furnace may take as much as 6,000,000 Btu per ton of charge depending on the moisture contents, and the waste-heat boilers recover about 50 per cent or more of the heat.

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Chapter 5

Anode Furnace Refining

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and
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The production of copper anodes began about 1865 in Europe and was necessitated by the development of the electrolytic refining of copper. Early anodes produced were small compared to modern standards, averaging about 18 inches square, less than 1 inch thick, and weighed approximately 75 pounds (Figure 5-1). Over the years many different sizes and shapes have been made to suit the requirements of the electrolytic refiners. Normally, the anodes required for both the series and multiple systems of electrolytic refining have been obtained by casting methods, but hot rolling of large cast blocks was adopted for one series system in use for many years, and only recently abandoned.

During the past thirty years a transition has been made in the molten

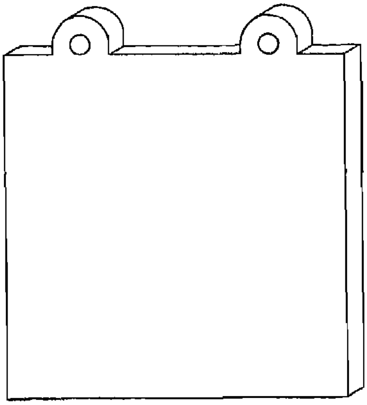

FIGURE 5-1. Typical early anode used in Europe.

metal preparation procedures for anode casting; almost half of the anode production is now derived from molten blister, whereas previously most of the production was by remelting and refining of blister cakes. Recently (1950) an electric arc furnace was installed in one refinery for the preparation of anode metal from tankhouse anode scrap. More details will be given later on these important metal preparation methods as they exist today in the copper industry.

The objective in furnace refining and casting of anode copper is to produce, within economic standards, an anode which is both chemically and physically within tolerance for good electrolytic refining practice. The process of anode production consists of the following operations in order of sequence. The total time required for a complete cycle is usually 24 hours.

(1) Calculation of the necessary blend of materials to produce the final required analyses of the anode from the impure copper available.

(2) Charging the furnace.

(3) Melting the furnace charge in required time.

(4) Skimming slag from surface of molten bath.

(5) Oxidizing (refining) the molten metal by introduction of air through blowpipes.

(6) Final skimming of residual slag or oxides.

(7) Poling the metal bath, or reducing the oxides formed during the refining phase, by the use of coke, charcoal, and green wood poles for agitation of the metal bath.

(8) Casting the refined metal into anodes.

The shape and weight of an anode is predicated by one or more of the following factors:

(1) The process, *i.e.*, whether series or multiple.

(2) The impurity or precious-metal content.

(3) The power efficiency of the electrolytic system.

(4) Power costs.

The multiple process anodes, weighing from 500 to 800 pounds, are rectangular or square in shape and are cast with lugs on the top ends for purposes of hanging and electrical contact. The contact lugs are of various types, being designed for power efficiency, simplicity of casting, and ease of release from the mold (Figure 5-2).

At present, in the United States, the greatest production of anodes is in the form shown in Figures 5-2 and 5-3, and only one refinery is now producing electrolytic copper from a cast anode for the series system (Figure 5-4). Figure 5-3 is a multiple-process anode weighing between 675 and 800 pounds, approximately 36 inches wide, from 37 to 41 inches long, 1¾ to 2 inches thick, and has the special grooved (Baltimore)

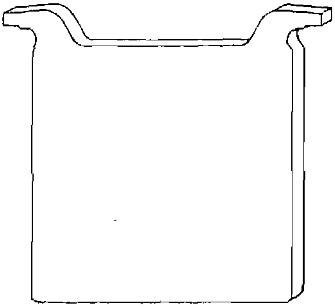

FIGURE 5-2. Regular type of anode made for ease of casting.

contact lug in order to keep electrical power losses to a minimum. In the series process the anode is usually rectangular in shape (Figure 5-4), and weighs approximately 100 to 150 pounds.

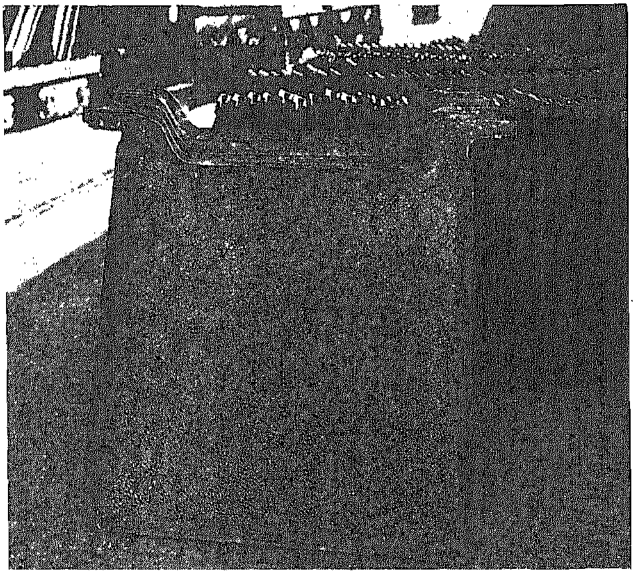

FIGURE 5-3. Baltimore type of anode with grooved contact lug. Its feature is low contact voltage losses. More anodes are being cast of this type than any other.

Furnace Refining

Metallurgically, the process is one which employs oxidation, fluxing, and reduction, although only simple oxidation and reduction are employed in most refineries.

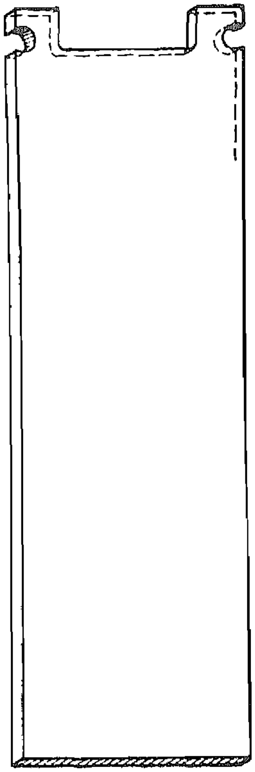

FIGURE 5-4. Hand-cast series anode, approximately 12 inches wide, 54 inches long, ⅝ inch thick, and weighing approximately 115 pounds.

The basis of the anode-refining operation is the weak affinity between oxygen and copper as contrasted to that between oxygen and the impurities. The practice is to introduce compressed air at 8 to 10 pounds pressure through iron pipes, one end being submerged under the molten metal surface, the bubbling action agitating the molten metal, bringing the newly disturbed surface of the copper in contact with the furnace atmosphere, and thus forming copper oxide. The copper oxide (Cu_2O) dissolves in the copper bath, reacts with the copper sulfide present, and forms SO_2 which is evolved from the metal bath, while due to the scorifying action of the Cu_2O other metallic oxides are formed which combine with added silica to form a slag. The order in which the impurities in copper are removed by fire-refining methods is: sulfur, zinc, tin, and iron, these being almost entirely eliminated by oxidation; in addition, a partial elimination of many other impurities is effected. Lead, arsenic, and antimony can only be eliminated in large quantities by fluxing. Oxygen is removed by reduction. Some impurities, such as nickel, bismuth, selenium, and tellurium resist oxidizing fire-refining treatments almost completely. It is possible to effect an elimination of some of these elements, but not economically or in a practical manner; they must be eliminated by electrolysis.

In order to be able to produce an anode of suitable physical shape for use in the refinery, it is important that the "set" or exposed surface of the casting be flat, and also that the supporting lugs be of sufficient strength to resist fracture due to the shock loads of the handling methods employed.

The impure "blister" copper derives its name from the large blisters on the cast surface which are produced by the liberation of SO_2 and other gases, just under the first congealed metal surface. The gases liberated cause swellings or blisters to form, making this quality of metal entirely unsuitable for the production of the desired flat-surface anode. The introduction of oxygen into the metal bath, by means of the air pipes, eliminates the excessive amounts of sulfur, and at the same time any zinc and tin present are largely eliminated. The elimination of the zinc would have been required in any event since the presence of this element indicates incomplete refining, a practice which is largely responsible for breaking of the supporting lugs when the anodes are being transported.

Claims have been made that a high lead content or a high total impurity content cause weak lugs, but no difficulty has been encountered on anodes containing as much as 0.45 per cent Pb, and having a copper content as low as 98 per cent. One such charge from which anodes of normal physical quality were produced was of the following analysis: 98 per cent Cu, 0.452 Pb, 0.62 Ni, 0.198 Sb, 0.220 As.

The removal of lead and whatever residual tin is left in the oxidized metal may be accomplished by fluxing the oxidized molten bath with a layer of fused silica. The silica is either added in batches of 1 to 3 tons directly on the molten bath, preferably in fine powder form, or introduced through an injector below the surface of the metal bath. Upon becoming semifluid it slowly reacts with the lead and residual tin, while the bath is being agitated with air, to form a lead-tin-copper silicate slag. This slag is skimmed from the surface of the metal. Another batch of silica is then added if further fluxing is necessary.

The surface of the metal bath is then partially covered with coke, and logs of green wood are introduced to expedite the reduction of the oxygen to about 0.1 per cent. The green wood is used to agitate thoroughly the metal in contact with the coke on the surface of the metal bath, and also assists in the reduction process as the furnace and metal temperatures char the wood and produce reducing gases.

The removal of arsenic and antimony may be accomplished by the fluxing action of soda ash, which is introduced, agitated, and then removed in the same manner as in the silica treatment. The efficiency of the fluxes on high-impurity burdens is good, and their use permits much greater flexibility of operation than would otherwise be possible. The efficiency of the fluxes on small amounts of impurities, however, is very poor, and complete removal is rarely, if ever, carried out in anode manufacture.

The Furnace Charge and the Resultant Anode

Because of the expense entailed in fluxing operations, due to the resmelting cost of the slags produced, and to the excessive corrosion of the refractory furnace lining, every effort is made to produce a suitable anode by blending the pure and the impure blisters in each furnace charge.

Table 5-1 lists the typical analyses of various blister coppers, black coppers produced from slags, scrap from junkyards, mill scales, and other forms of copper source material which may be part of the blended charge to an anode furnace. A furnace charge will also usually contain the available production of anode scrap from the electrolytic refinery.

TABLE 5-1. ANALYSES OF VARIOUS TYPES OF COPPER FOR THE ANODE FURNACE

Blisters	Oz. Per Ton		Per Cent									
	Au	Ag	Cu	Pb	Sn	Zn	Bi	As	Sb	Ni	Se	Te
1	0.01	2.4	99.1	0.01	Nil	Nil	0.00005	0.01	0.004	0.003	0.005	0.01
2	.06	7.5	99.2	.015	"	"	.0003	.01	.005	.05	.04	.01
3	1.25	5.9	99.0	.008	"	"	.00003	.02	.005	.008	.007	.015
4	1.4	18.6	98.6	.05	"	"	.0015	.10	.03	.06	.04	.03
5	1.3	42.0	98.8	.15	"	"	.002	.15	.01	.30	.21	.01
6	3.2	195.0	96.1	.10	"	"	.001	.40	.25	.40	.30	.04
Black Coppers												
1	0.15	6.9	91.1	0.83	1.85	0.40	0.001	0.12	0.09	1.27		
2	.68	7.2	94.75	.55	.70	.35	.0015	.12	.18	.64		
3	2.28	29.7	94.13	.75	.10	Nil	....	.22	.60	3.77		
4	.02	8.4	96.52	1.00	.09	Nil	....	.04	.13	1.50		
Miscellaneous												
1	....	....	96-99	0.1	0.05	....	....	....	....	0.1		
2	....	....	93.5-96.5	1.0	.40	0.25	....	....	0.01	.5		
3	....	....	90.0-94.0	2.0	1.0	.5	....	....	.1	1.0		

It is evident from the above compositions that to limit the anode furnace refining operation to the simple oxidation and reduction process, it becomes necessary to blend carefully the various compositions, limiting the use of the compositions assaying less than 98 per cent copper.

This, of course, can be accomplished only when sufficient quantities of crudes of diluent quality are available. Table 5-2 gives some of the more typical compositions of cast anodes. It is clearly evident that some anodes are prepared simply from a single blister, while others are a blend of "clean" and "foul" blisters. The anodes tabulated are representative of typical impurity contents and were produced from American and foreign blisters, as well as from other copper sources.

TABLE 5-2. ANALYSES OF ANODES

	Oz. Per Ton		Per Cent								
Anodes	Au	Ag	Cu	Pb	Fe	Bi	As	Sb	Ni	Se	Te
1	0.01	2.40	99.60	0.01	0.06	0.0005	0.02	0.004	0.002	0.01	0.006
2	.06	7.5	99.55	.02	.024	.0001	.01	.01	.045	.04	.01
3	1.25	7.5	99.50	.012	.03	.0001	.004	.002	.018	.03	.01
4	.60	33.0	99.50	.013	.025	.001	.006	.005	.04	.03	.02
5	1.10	45.0	98.82	.18	.01	.0015	.15	.05	.25	.11	.06
6	2.10	58.0	98.65	.18	.012	.001	.16	.08	.28	.06	.02
7	3.5	91.0	98.51	.22	.015	.0015	.32	.24	.35	.05	.02
8	1.4	74.0	98.50	.32	.01	.001	.19	.06	.30	.15	.05
9	1.5	50.6	98.65	.19	.01	.001	.05	.04	.60	.20	.05
10	3.6	78.0	98.85	.08	.02	.009	.10	.17	.32	.05	.08

The above anode compositions are being electrolyzed in large tonnages.

Furnace Types and Use of Refractories

Anode copper refining employs two types of fuel-fired furnaces: a cylindrical furnace, which is usually located in close proximity to the converters and takes a liquid metal charge, and a reverberatory furnace designed to remelt and refine solid blister copper or other forms of solid copper-bearing material. With the exception of charging and melting, all other operations are comparable. Where anode copper refining in the furnace is not necessary and only melting is required, electric arc furnaces can be used if cheap power is available.

One refinery is transporting liquid blister via a liquid metal car over a considerable distance. This is accomplished by providing a sufficiently well-insulated container to permit the transfer to be effected without serious loss of super-heat. The design of this plant was based on the successful accomplishment of liquid metal transfer, as better economies in operating cost could be obtained in this instance if the smelting operations were located at some distance from the refining plant.

The types of fuel used are pulverized coal, natural gas, fuel oil, and electric power. Western refineries generally use gas when available, with oil as a standby, while eastern refineries must use oil or coal. Coal is not a desirable fuel and has been almost entirely replaced by oil.

Cylindrical furnaces are built in capacities of 150 to 200 tons. At the top of the furnace, on the end opposite the oil burners, a mouth is provided through which molten blister copper is poured and through which the combustion gases pass to the flue or directly to the atmosphere. The air pipe for oxidation, the poles for reduction, as well as the skimming tools are inserted through an opening in the side of the furnace. A tapping spout is provided on the opposite or casting side of the furnace. These furnaces rest on steel rollers and are rotated through an arc of about 45 degrees by a ring gear and motor-driven pinion.

Reverberatory furnaces are built in capacities ranging from 200 to 400 tons. This type of furnace is built on brick or concrete piers, so spaced as to allow for ventilation and cooling of the bottom by natural draft, and for the placement of tie rods. In some cases the foundation is made of a block of solid concrete, provided with ducts for placement of tie rods and other ducts for fan cooling. In order to form the bottom, concrete is laid and formed to give the desired shape. For brick bottoms the inverted arch is the general pattern and a tapping slot is provided in either the side or the end of the furnace, depending on the plant layout. Some refineries are still using sand bottoms, but brick is usually preferred. The shell is of steel supported by buckstays, which in turn are tied in, top and bottom, both sidewise and lengthwise by tie rods. Over the charging doors and supporting the sprung roof are copper or steel water-jacketed skewbacks. Generally, three charging doors are provided for the larger furnaces.

A plant which has liquid blister available and also processes solid blister may have both cylindrical furnaces and reverberatories. The liquid blister is always charged to the cylindrical furnaces, but any excess may be added to the cold-charge reverberatory furnace at the beginning of the charging period or following the melting of the solid charge.

The refractories used for the construction of the linings for the various types of furnaces employed in the production of refined anode metal vary widely from plant to plant depending on the individual metallurgical problems, and whether the source of metal is liquid blister or solid materials.

In the handling of liquid blister by the cylindrical tilting furnaces, the refractories are exposed to far less slagging action, and particularly to less extremes of alternate heating and cooling than in the case of reverberatories. The general practice is therefore to use a basic lining, either of burned or unburned chemically bonded magnesite brick. This type of brick is most resistant to slagging actions and in this type of service, its tendency to spall does not become a serious problem since temperature fluctuations are not severe. Accordingly, the practice is to endeavor to keep the temperature differential across the lining as small as possible by use of insulation so as to reduce strains. At the same time a considerable saving in fuel is also obtained. Cylindrical furnaces so constructed and maintained by occasional spray-coating of a replacement refractory have been in continuous service for as long as 7 to 10 years before a complete replacement of the lining was required.

In the reverberatory type of melting furnace, the service requirements of the lining vary from medium to severe. Medium service conditions are usually present in those plants having a relatively pure form of blister copper as the furnace charge. Severe service conditions are the result of anode charges being largely composed of various forms of scrap and impure blisters. The reverberatory furnaces, therefore, vary from a construction using basic brick in bottom and side walls, with a silica brick roof, to a lighter duty construction having a silica bottom (either sand or brick) and upper side walls and roof of silica as well.

Excellent progress has been made in the maintenance of furnace refractories by spray or "gun" applications of refractory patching materials in order to extend service life between repairs. Two methods of application are used. One method is to apply a premixed slurry by means of a pressurized blowcase forcing the liquid through a simple nozzle which sprays the material on the hot refractory surface to be repaired. The other, more recent method for the maintenance of basic furnace side walls, avoids the use of a premixed slurry by a special type of gun, which continuously ejects a dry preground basic grit which is wet by a built-in water spray ring near the exit of the applying nozzle. Certain advantages are inherent in this type of applicator, since no premixing equipment is required, and the moisture content of the mixture can be instantly altered by the operator to suit the individual furnace conditions. As a result of the application of a premixed silica slurry to a silica roof, its life can be extended from about 125 charges to as much as 500 charges. Similar increases in the life of basic side walls can be expected from the use of suitable patching materials applied by gun application.

Refractory service in the electric arc furnaces is most severe of all, and in fact refractory life limits the melting rate of the furnace. Basic brick are now used for the entire lining, but the earlier installations in the copper industry used a monolithic burned magnesite bottom. The severity of service is due to the extremely high temperatures resulting from the arcs.

Plant Design

A typical layout for a unit operating on liquid blister will place two cylindrical furnaces at right angles to each other, to serve one anode casting wheel centered between them (Figure 5-5). The wheel is operated both clockwise and counterclockwise, receiving service first from one furnace and then the other. While one furnace charge is being refined, the other furnace charge is being cast. This particular layout allows the almost continuous supply of molten blister from the smelting furnaces to be poured promptly into a waiting furnace. The installation cost of this type of plant is much lower than the reverberatory, per ton of anodes produced, since the two furnaces and one casting wheel are in operation 20 to 22 hours per day.

The most prevalent plant design for a reverberatory furnace installation locates the furnaces on a line passing through the longitudinal axis of the furnaces. Another scheme places the furnaces parallel to each other. In the longitudinal alignment, charging of the furnace is accomplished from a common charging aisle served by a narrow-gage track system, and casting wheels are located on the opposite side of the

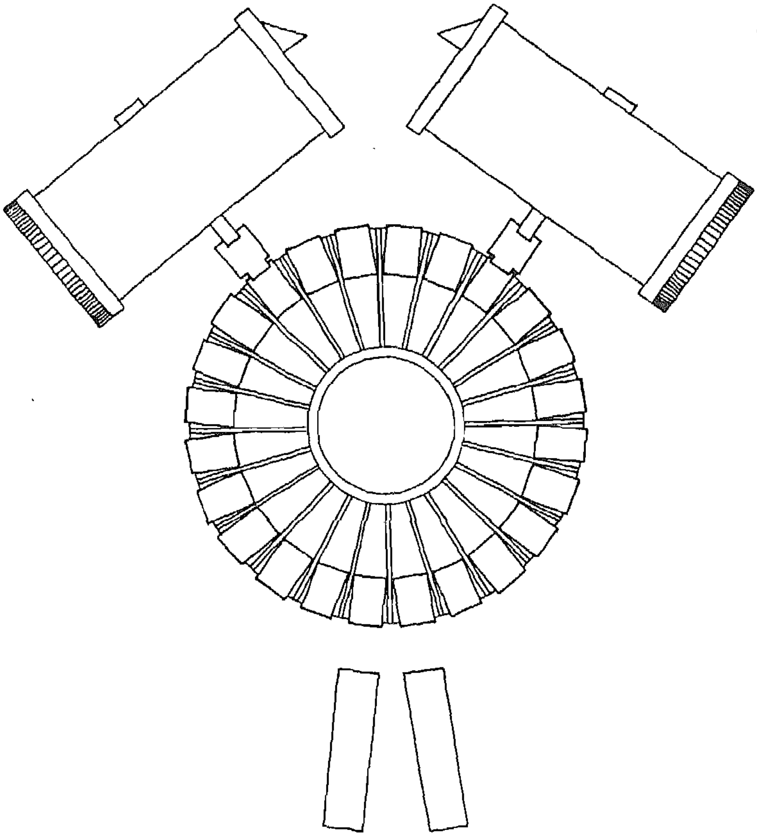

FIGURE 5-5. General layout used for cylindrical casting furnace plants.

furnace. The molten metal is supplied from a taphole located in the casting side. The parallel arrangement requires delivery of blister by overhead crane to a charging area which is common to only two adjacent furnaces, and the casting wheel and metal taphole are located at one end of the furnace instead of the side.

When an electric arc furnace is used for the remelting of anode scrap from the electrolytic tank-house, it is located adjacent to the casting wheel and with sufficient elevation to allow a gravity flow of the metal down a launder or refractory-lined trough to the ladle.

Charging the Furnace

In the operation of cylindrical furnaces, the charging time is very important and must be held within the limits required to maintain an efficient furnace cycle. For this reason large ladles, refractory-lined, having capacities ranging from 30 to 50 tons are used. These ladles receive molten blister copper directly from the converters, or in some cases from an intermediate holding furnace of 250 to 300 tons capacity, as necessitated either by nonuniform delivery of liquid blister from the smelting furnaces or by fluctuating anode casting rates. The ladles are filled and then transferred to the anode refining aisle by overhead cranes or self-propelled transfer cars. At this point they are picked up by charging-aisle cranes and delivered to the anode refining furnace. While one ladle is being delivered, another is being filled.

The objectives in the charging operation of reverberatory furnaces are:

(1) To minimize the heat loss during charging.

(2) To obtain maximum initial input.

(3) To keep the charging time as short as possible in order to maintain the furnace cycle on a 24-hour basis.

The method of charging is basically the same in all large refineries handling solid metal. Electric charging machines with wide maneuverability and having a lifting capacity up to 5 tons are used (Figure 5-6). These machines are served with blister copper, scrap copper, returns, etc., by a narrow-gage rail system or by overhead electric cranes. The furnace is charged, beginning at the bridge, or burner end of the furnace, working toward one door at a time, and returning to the bridge end to complete the charge if scrap copper or other bulky material has been previously charged. The charging rate for blister copper is approximately 125 tons per hour, and for scrap copper approximately 50 tons per hour. The scrap copper delivered to the anode furnace is a heterogeneous mixture of bundles weighing from 150 to 2,000 pounds. Loose material is handled in self-emptying chargeboxes wherever possible in order to facilitate charging, or compressed into briquettes or bales at a preparation area.

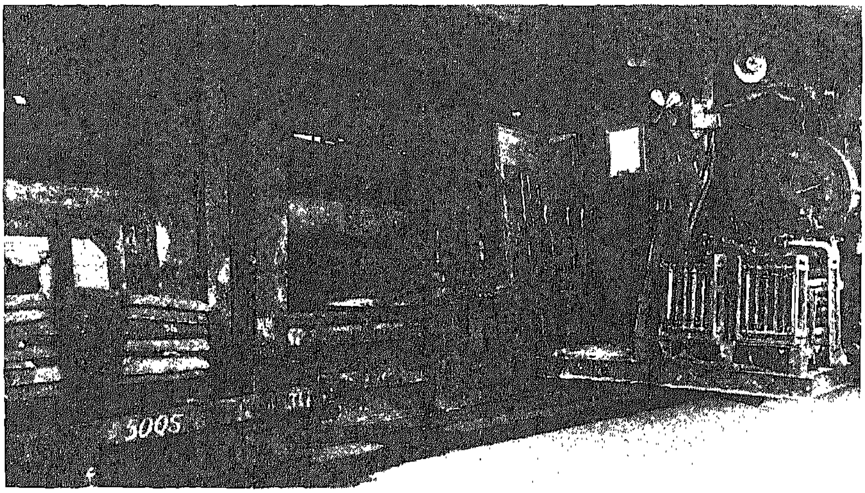

FIGURE 5-6. *Charging machine capable of multi-directional movement. The blister copper on the charging "peel" weighs approximately 3 tons.*

The charge machinery for an electric arc furnace is usually a simple feeding mechanism capable of handling the relatively light anode scrap (compared to heavy blister blocks) and thrusting the anode scrap through a refractory-lined slot in the upper wall of the furnace. The charging rate must be nearly equal to the melting and casting rates, as this type of furnace has small metal capacity compared with fuel-fired furnaces, and has no refining cycle.

Melting and Skimming

Cylindrical furnaces receiving molten metal do not, as in the case of reverberatories, have a melting operation. The metal temperature is lowered or raised according to the temperature condition in the furnace when it is filled to capacity.

The melting operation in a reverberatory furnace has for its objective efficiency in fuel consumption while still maintaining a reasonable melting cycle. The cooling of the furnace walls during the charging period has a very deterrent effect on the melting operation. A furnace pressure neutral to slightly negative enhances the melting operation. This, of course, is dependent on the draft available. For assistance in combustion of the fuel, furnaces are provided with blowers delivering up to 10,000 cubic feet of air per minute. Gas analyses from samples taken in the furnace under the verb arch are used to determine the combustion efficiency. The melting cycle is continued until the charge is "flat" (*i.e.*, completely liquid on the surface and to a considerable depth), and at times continued until indications are that the charge is "afloat" or "off bottom" (*i.e.*, completely and thoroughly melted to the bottom). The amount of slag formed depends on the content of impurities in the metal charged; where a considerable amount of slag has formed during the melting cycle, the skimming operation begins when the charge is "flat," as otherwise too great a quantity of slag would accumulate on the surface of the bath, and impede the heat transfer to the metal.

There is a decided increase in the slag produced when a furnace is fired with powdered coal; on the other hand, fuel oil or gas has no tendency to increase the amount of slag formed. Clean blister-copper charges produce approximately 1½ per cent slag, while blended charges containing foul blisters will produce approximately 3 per cent slag. Very foul charges may produce as high as 25 per cent slag.

The skimming operation in the case of cylindrical furnaces is carried on during the latter part of the charging period and is completed shortly after the furnace has been filled. Reverberatories, on the other hand, are skimmed as previously mentioned, when "flat" or when "off bottom." This is accomplished by using long-handled steel rabbles, or hoes, skimming the slag from the surface of the metal into steel or cast-iron slag pans, having approximately a 2-ton capacity. In the case of the cylindrical furnace, the slag is skimmed into ladles and returned to the converters. The slag from the reverberatory furnace is cooled, broken or crushed, and delivered to blast furnaces for reduction to black copper.

In comparison, the slag production of an electric melting furnace is very low, since no refining is done, as the scrap anode metal charged has already been refined once. Skimming of the slag is therefore very infrequent, and is only necessary when a reduction of the melting rate is noted.

Oxidation or "Blowing"

The oxidation of the copper charge usually begins when the charge is "off bottom." Generally the air pipes for agitation of the bath are put in the charge when the furnace is opened for skimming, and blowing is continued from that point on, even though the "off bottom" stage has not arrived. In some cases the metal in the bath may be skimmed clean of slag and the furnace then closed up again for further melting, while in others melting is continued until the "off bottom" stage is reached before opening the furnace for skimming. The efficiency of the blowing cycle is enhanced by (1) a totally melted charge, (2) a negative furnace pressure, (3) a highly oxidizing furnace atmosphere, (4) controlled metal temperature, (5) maintenance of a well-skimmed bath, (6) the use of a sufficient number of pipes in order to keep the entire surface of the metal bath turbulent.

Samples of the molten metal are taken periodically with a "say ladle" (a small steel ladle, 1½ inches in diameter, 1 inch deep, with a long handle) which is dipped into the bath and a test button taken to show the state of the metal. Charges of extremely high sulfur content will expel copper from the test button upon cooling, leaving only a solidified shell of metal in the "say ladle." As blowing progresses, the solidifying test button shows a break in the "set" which "throws a worm" (*i.e.*, gases expelling last of liquid metal from under the frozen surface of the sample). These samples are indicative of high sulfur content. The general practice, when the above condition prevails, is to employ what is called a "poling down" operation. One end of a green wood pole of moderate size is forced under the bath, by anchoring the pole at its midway point and raising the other end with a chain-block. This violent agitation caused by the conversion of the sap in the wood to steam, in addition to that of the blowpipes, speeds up the liberation of sulfur from the copper bath. When the test button shows the disappearance of the "worm," oxidation is continued with agitation by air until the test button shows a depression in the center of the "set" surface. At this point, oxidation ends. However, if further refining is necessary for the removal of lead, arsenic, or antimony, then the fluxing operation may require further oxidation in order to raise the oxygen content closer to 1 per cent. For lead removal alone, the fluxing may be started sooner, or at a point closer to 0.5 per cent oxygen.

Poling

When the charge has been refined by oxidation, or fluxing as well, the bath is skimmed clean, the pipes removed, and the furnace openings closed and luted. The surface of the bath is then covered with coke and poling begins. The general practice in poling is to use hardwood poles, although softwood poles may be used, but not without objection due to the greater number required. Strong poling action is continued until the test button shows a dark spot in the set surface, after which poling is continued more cautiously until the disappearance of the spot and the set surface on the test button comes to a flat or slightly raised surface. At this point the metal is ready to be cast. During the casting period some additional poling may be required to maintain the desired set.

Casting

The casting of anodes is accomplished by tapping the metal in a continuous stream into a casting ladle and bringing the molds to the pouring position under the ladle. There are many differences in the type of casting machine, the type of ladle, the kind of mold, the method of anode removal from the mold, and other minor details of operation.

Casting machines are of two types. The conventional type (Figure 5-7) is a wheel carrying from 16 to 28 molds and driven by hydraulic means or by electric motors. The larger wheels normally cast at high rates. These wheels are used either by a "stop to cast" method or on a basis which allows for continuous movement of the molds under the ladle. The other type of casting machine is a straight-line conveyor with the molds fastened to it. The direction of movement is parallel to the length of the furnace. In both cases the anode is carried to the take-off position, where it is removed by means of an air lift or by an electric crane designed for this purpose.

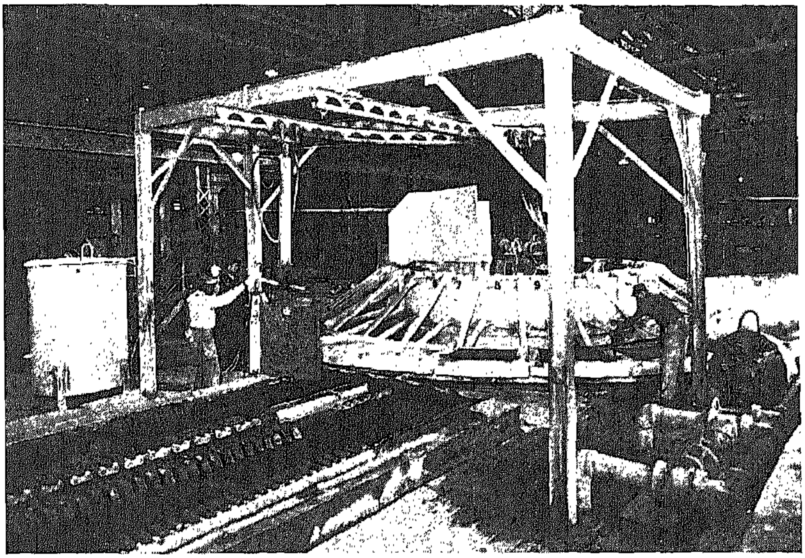

FIGURE 5-7. Large (28-mold) casting wheel capable of casting 75 to 85 tons per hour. Anodes are removed from the molds by means of an air lift and lowered to cooling boshes. This is a continuously moving wheel.

There are two types of ladles, the end-pour and the side-pour ladle. The former may be an open-end type where the metal flows over the refractory-coated end wall, or it may be provided with a detachable deflector which directs the metal stream downward. These ladles will cast anodes at the rate of 50 to 55 tons per hour. Higher casting speeds are attained by using two ladles. The multiple-spout side-pour ladle is designed for casting anodes on a wheel which is in constant motion.

The casting rate is 50 to 55 tons per hour for one ladle, and when two are used, pouring into a common mold, speeds up to 85 tons an hour can be attained. (Figure 5-8). All ladles are brick-lined and shaped in final form by a cement and sand mixture. The ladle shells are of steel or cast iron, with steel construction being preferred.

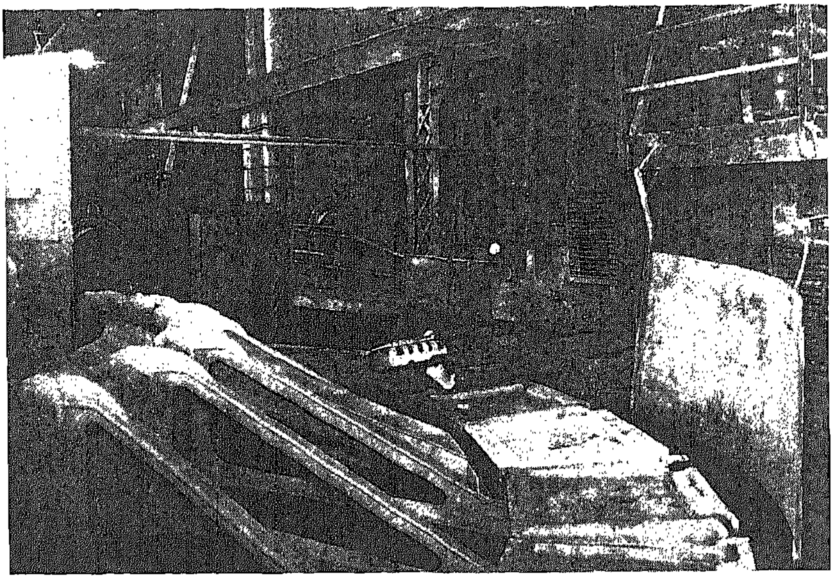

FIGURE 5-8. Multiple-spout side-pour ladles used with casting wheel of Figure 5-7. The metal streams pour towards each other into the same mold.

Anode molds are generally made of copper, although in some cases it has been found economical to make them of cast iron. The anode refining units that do not have refined copper available make their molds of anode copper. Molds made of refined copper are superior to those of cast iron or of anode copper in their heat-transfer rate, which produces a more rapid rate of chill. They also possess more rapid adjustability to the desired temperature for application of mold wash, and of course, have longer life.

The usual type of anode mold is provided with a lifting pin having a tapered head flush with the surface of the mold; the opposite end rides on a cam track which raises the pin, and lifts one side of the anode from the mold, so that the cast lugs may be engaged by a lifting mechanism. The weight of an anode mold varies from 3,500 to 5,000 pounds. The tendency is toward heavier molds where the cooling application between the casting point and the take-off point is at a minimum. On the other hand, where the rate of cooling is extremely rapid between these points, lighter molds are the preferred practice. Rapid cooling produces severe warpage of the molds, so that lighter molds are preferred since they are more easily straightened when warped. Molds tend to warp in the direction of contact with the coolant.

Cooling of the anode molds is primarily dependent on the size of casting wheel and the rate of casting. Where the wheel is of large size compared to the casting rate (*i.e.*, 22 to 24 molds for 30 to 40 tons per hour), very little water cooling is needed and it is usually applied by a simple spray to the top or bottom of the mold surface. Where casting rates are high, multiple sprays are used both on the top and bottom of the molds.

In anode casting operations which employ a minimum of mold cooling between the casting and take-off points, the mold wash is a water slurry of alunite or silica, or a solution of bentonite. The application of mold wash not only insulates the mold but also acts as a partial coolant. Where bentonite alone is used, a clay or alunite slurry is brushed on the mold at the point of metal impingement for increased protection for prevention of fusion of the anode to the mold. This slurry is also applied to the heads of the lifting pins, which are a part of the mold surface exposed to the molten metal.

The type of casting operation that requires a uniform mold-wash application uses an alunite or silica slurry of predetermined viscosity which is sprayed on the mold with a Murphy spray gun. The pins are luted with a clay slurry. This controlled application of a uniform mold wash is a necessity with the use of the single or multiple-spout side-pour ladle.

Pouring copper to make an anode requires a reasonably uniform metal temperature and skillful manipulation of the ladle. The preferred casting temperature is approximately 1120°C (2050°F) plus or minus 5°C or 10°F. Unless compensated for by a fast pouring rate, temperatures below 1115°C (2040°F) will give difficulty in forming the lugs in the anode. Temperatures above 1125°C (2060°F) will tend to cause fusion of the anode to the mold, particularly so in the "stop to cast" method where metal impingement is limited to a small area of the mold surface.

The ladles are actuated by controls located in the ladle operator's house. Hydraulic systems are used for controlling the raising or lowering of the ladles, as well as variable speed motor-operated electric hoist drives. Generally the operator's house is located on the side of the wheel, but in the case of the dual side-pour ladles, the house is located over the hub of the wheel for better observation of the metal entering the mold.

The physical qualities of the anode required by the electrolytic refiners are uniform thickness and weight, freedom from sharp or raised edges and fins, a minimum of embedded foreign materials, and an absence of objectional blisters or other protrusions. These qualities are under the direct control of the casting operator, except for surface blisters, which are due to inadequate refining and sulfur elimination. In some instances, a shield placed a few inches above the surface of the cast anode, preventing rapid solidification of the surface of the anode, is helpful in minimizing blister formation.

In order to pour an anode of uniform thickness, it is necessary that a suitable mark in the mold be clearly visible to the ladle operator. These marks may be chiseled in the mold or cast in at the time of manufacture. For the operation of refineries that do not require changes in the thickness of the anode, it is common to make the depth of the molds to the exact thickness of the anode desired. It is also imperative that warped molds be replaced immediately.

Edges on the cast anode are the result of improper manipulation of the ladle, mechanical difficulty with the wheel, or to quick starting of the wheel, following the pouring of the metal, and before solidification of the anode. They may also result from the improper application of mold wash on the sides of the mold. Fins on the lower side of the anode result from cracks in the molds. The general practice is to close these cracks by peening as soon as they develop. When the cracks are beyond repair by this method the mold is replaced.

A bridge is located in the body of the casting ladle for the purpose of preventing floating foreign material from flowing with the metal stream. Another source of embedded material is the mold wash. Proper control of the viscosity of the mold wash, with respect to the mold temperature, will tend to prevent this.

Removal of Anodes

One method of removal of the anode from the mold is shown in Figure 5-7 where a manually operated air lift is used for engagement of a tong under the anode lugs, to allow the anode to be raised from the mold and lowered to the cooling bosh tanks. This manual method is very flexible and rapid, particularly so for the continuously moving type of wheel operating at high casting rates.

The cooling tanks are located under the anode lift mechanism and are from 9 to 20 molds from the anode pouring position, depending on the diameter of the wheel. The sides of the tanks are usually slotted in order to space the anodes uniformly. Some refineries have abandoned the stationary slotted side, having substituted an electrically driven slotted chain, which receives the anode at the end of the tank nearest to the mold, and then progressively moves the anodes toward the rear of the tank. High production rates can be handled by this construction since the full length of the tank is not traversed. Anodes are removed from the cooling tanks by a suitable rack provided with the required number of suspended hooks to receive anodes as spaced on the chain in the tank.

The tendency in the industry is to replace the manual method with mechanically operated tongs, operated by air cylinders remotely controlled, or in some cases by a small electrically controlled crane. None of the mechanically operated systems in use appear to be capable of handling over 55 to 60 tons per hour, but most systems are not called upon to handle more than 30 to 40 tons per hour from a "stop to cast" type of wheel. The wheel is always stopped at a predetermined point which coincides with placement of the tongs.

The pick-up mechanism used on the "straight line" type of casting machine is capable of very high rates, but it does not place the anodes *in a cooling tank, which is desirable to facilitate removal of the oxidized* surface or adherent mold wash.

Inspection of the anodes in some instances is accomplished prior to placement of anodes in the cooling tank, while in other instances the inspection follows their removal. In all cases the anodes are trimmed (*i.e.*, chipped with pneumatic tools for removal of edges and fins) prior to delivery to the electrolytic refinery via narrow-gage or standard-gage railroad cars.

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Chapter 6

Copper Slags and Mattes

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Our knowledge of slags and mattes, until very recently, was derived almost wholly from a study of the solid products and a general observation of the behavior of the molten charge in the furnace. The information thus gained has enabled the metallurgists and operators to attain high smelting rates and good recoveries at low costs.

Equilibrium diagrams of SiO_2-FeO, SiO_2-CaO, etc., as well as those of Cu_2S-FeS, Cu_2S-Ni_3S_2, etc., have been established and have proved helpful even though it is now believed that the compounds which separate on cooling did not necessarily exist as such in the molten state. The classic work of Vogt in which numerous well-known minerals were identified in slags has been summarized by Fulton[1].

The wealth of knowledge regarding aqueous solutions built up by physical chemists and the methods used in this work have only recently been applied to igneous solutions, with special applications thus far to open-hearth steel slags. Schuhmann[2] has pointed out the importance of applying the laws of physical chemistry and thermodynamics to copper metallurgy and suggests a program of research to this end, but only a start has been made.

In order to present a complete picture it will be necessary in this chapter to take account of the large amount of practical knowledge which has been accumulated regarding slags and mattes and supplement it by the rather meager scientific facts which have thus far become available by more recent theoretical considerations.

COPPER SLAGS

In the production of copper from ores and concentrates there are four operations in which slag is produced:

(1) Primary smelting of the ores and concentrates.

(2) Converting the copper matte to blister copper.

(3) Refining the blister copper to produce anodes, or in a few cases ingots for market.

(4) Melting cathodes to produce wirebars or other finished shapes. In a completely integrated plant where all these operations are performed the slags from (3) and (4) are returned to operations (2) or (1) and the slag from (2) is returned to (1). For convenience, therefore, the slags will be discussed in the reverse order.

Refinery Slags

Operations (3) and (4) above are essentially the same, the slag in each case being produced during the blowing period in which the charge of molten copper is oxidized by air to the "set copper" condition approximating the eutectic of copper and cuprous oxide. At this point the slag which has formed must be carefully removed to prevent the oxidized impurities from being reduced and recontaminating the copper in the poling operation that follows.

Since only a very small fraction of a per cent of oxidizable slag-forming impurities is present in cathode copper and only slightly more in blister copper, it is obvious that the slag produced will be relatively small in amount and will consist primarily of copper oxide from the bath, iron oxide from the blowing pipes and rabbles, and material from the lining of the furnace. At times a small amount of siliceous flux may be added to condition the slag for easy skimming, but no attempt is made to produce a slag of constant composition. Oxidizing the charge beyond the eutectic composition causes rapid increase in the amount of cuprous oxide taken into the slag and is therefore usually avoided.

There is a difference of opinion regarding the form in which cuprous oxide exists in slags. Copper silicate minerals are known in nature, but there is evidence that in slags there is no bond between the silica and the cuprous oxide and the cuprous oxide remains free in the fused bath or is combined as copper ferrite[8].

Refinery slags are too rich in copper and precious metals to be discarded. When the refining operation is carried out at a smelter or within economical shipping distance the slags are added as cold material to the converter or in some cases charged to the reverberatory furnace. If a smelter is not convenient the slags are accumulated and smelted periodically under strong reducing conditions in a cupola furnace to produce an impure metallic copper (black copper) which is returned to the anode furnace. The cupola slag is discarded.

Converter Slag

Copper matte from the primary smelting operation, consisting essentially of mixtures of Cu_2S and FeS in varying ratios, is blown with air in a converter to produce metallic copper (blister copper). In addition to the matte, other copper-bearing materials may be added for temperature control and copper recovery and siliceous ore or other siliceous materials are used as a flux.

There are two stages to the operation. In the first stage the iron is oxidized to FeO, joining the siliceous flux to form slag, and the sulfur associated with the iron is oxidized to SO_2. When tests show that this stage is completed the slag is removed, leaving what is essentially molten Cu_2S in the converter.

In the second stage the blowing is continued and oxidizes the sulfur preferentially to the copper. The operation is stopped when the removal of sulfur as SO_2 and SO_3 is completed, leaving the so-called blister copper in the converter.

Several practical considerations determine the composition of converter slag:

(1) Since the slag is to be charged to the reverberatory furnace its composition must be such as will blend with the primary reverberatory slag to give the latter the desired composition.

(2) The slag must be sufficiently fluid to pour satisfactorily from the converter to a ladle and from the ladle to the reverberatory furnace. In this connection it must be kept in mind that high temperatures must be avoided if damage to the converter lining is to be kept at a minimum.

(3) Since the converter lining is basic it would be attacked by highly siliceous slags. On the other hand, heat conservation is promoted by adding as much as possible of the cold siliceous flux to the converter where waste heat is available, rather than to the reverberatory furnace where fuel would be required to bring it up to temperature.

We have no definite proof regarding the mechanism of the reactions which take place during the slagging stage of the converter operation. It was formerly assumed that the iron in the original matte charge existed as the definite compound FeS in the liquid as well as the solid state, and that on oxidation to FeO it immediately united with the silica to form ferrous silicate. A physical chemist now would not express the process in these terms and would point to the relatively high electrical conductivity of ferrous silicate slags as proof of dissociation of the compounds. This concept of molten slags is discussed by Chipman and Chang[4] in their paper "The Ionic Nature of Metallurgical Slags. Simple Oxide Systems." Darken and Gurry[5, 6] have presented studies of the system iron-oxygen in two papers, following which Darken[7] has given a modern concept of the system Fe-Si-O. The most recent contribution to a knowledge of the Fe-Si-O system is the paper by Schuhmann and Ensio[8], "The Thermodynamics of Iron-silicate Slags: Slags Saturated with Gamma Iron." They present a table of the activities of FeO in various slags and derive the equilibrium diagram shown in Figure 6-1. This diagram, which differs little from those of other investigators, is of considerable importance since the iron silicates form the main constituent of copper smelting slags.

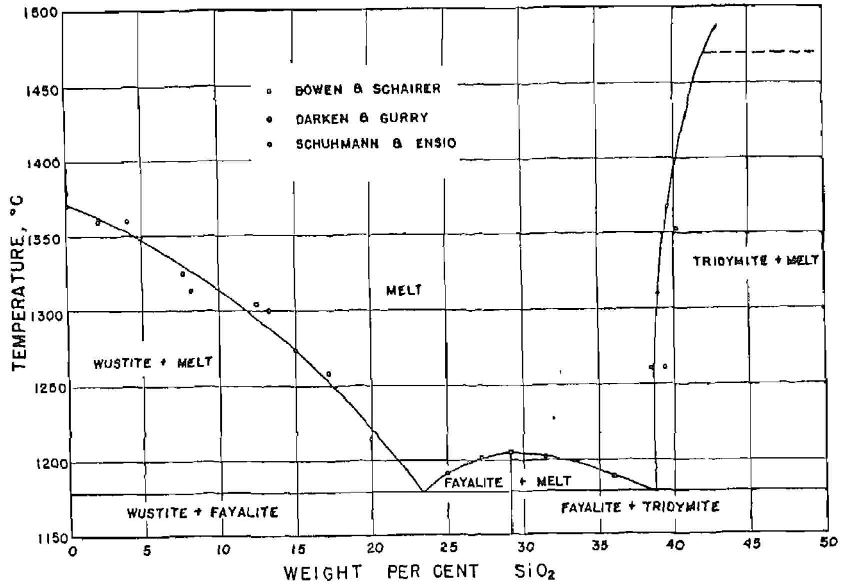

FIGURE 6-1. Phase diagram showing liquidus data for iron-silicate slags in equilibrium with solid iron. (*Courtesy of the American Institute of Mining and Metallurgical Engineers, Transactions.*)

As Schuhmann has stated, the designation of the components of copper slags is partly a matter of convenience. The iron silicate slags can be specified in terms of FeO, Fe_2O_3, and SiO_2; FeO, Fe_3O_4, and SiO_2; or Fe, O, and Si. Even though it may be departing from strict accuracy to refer to ferrous or ferric oxides and silicates as existing as such in the liquid state, it is convenient to speak of them as such in describing what takes place in the smelting operation and this practice will be followed in the subsequent discussion. FeO is a transition substance which reacts readily when it comes in contact with SiO_2, but is equally subject to further oxidation if silica is not immediately available. Under the conditions existing in the converter considerable amounts of ferric oxide are formed and dissolve in the slag. At temperatures approaching 1350°C the ferric oxide reacts with the matte and at times the evolution of SO_2 may become so rapid as to cause excessive boiling and frothing. The optimum temperature in a converter is such that the brick lining, which is always slightly cooler than the bath, becomes coated with Fe_3O_4-rich slag and is therefore protected from corrosion. At a lower temperature solid Fe_3O_4 tends to accumulate and remain behind when the slag is poured. At higher temperatures the reaction between Fe_3O_4 and matte occurs, causes the frothing previously mentioned, and exposes the bricks to both corrosion and erosion.

Converter linings are sometimes repaired by blowing matte with a deficiency of siliceous flux to produce an excessive amount of ferric iron in the slag, thus raising its melting point. The converter is then rotated so as to coat the brickwork with this sticky slag or allow it to solidify in badly corroded areas.

Converter slag carries considerable ferric oxide to the reverberatory furnace, where it becomes dissolved in both the matte and the slag. Its behavior there will be discussed later.

Reverberatory Furnace Slag

There are three general products from smelting and converting copper ores and concentrates:

(1) The blister copper from the converter, containing precious metals and small amounts of certain impurities. This is sent to the refinery and, as previously stated, the slag from refining operations is usually returned to the smelter and added either to the converter or reverberatory furnace charge.

(2) The gases, which in weight and bulk constitute the largest product. These are first cleaned of dust, which is returned to the smelting furnace, and the cleaned gas may be further treated to recover valuable products such as volatile oxides and sulfuric acid.

(3) The reverberatory slag, which is a composite of the converter slag, refinery slag, reverberatory fluxes, and all other slag-forming constituents which may be present in the charge.

The principal elements in the copper-bearing materials which come to a copper smelter are iron, sulfur, and copper, associated with which are minor quantities of refractory oxides such as SiO_2, Al_2O_3, CaO, MgO, etc.

As previously stated, the copper is recovered as metal and the sulfur is eliminated as gas. All the iron, regardless of its source, is removed in the reverberatory furnace slag either as ferrous silicate or dissolved Fe_3O_4. That part of the iron which temporarily enters the matte is, as already explained, oxidized in the converter and returned to the reverberatory furnace.

One of the chief problems of the copper plant metallurgist becomes the oxidizing and slagging of the iron with a minimum loss of copper.

The iron may be oxidized in a roasting furnace, in a copper converter, and to a minor extent in the reverberatory. Since there is never sufficient silica present to flux the iron oxide, more must be added in the converter or the reverberatory or both.

A large amount of iron oxide in the primary charge to the reverberatory furnace requires that a corresponding amount of silica be present in the charge or added to the reverberatory as flux. If a low-grade matte, high in Fe, is being produced a corresponding amount of SiO_2 must be added in the converter to flux the resulting FeO. The important thing to remember is that in any case all the iron and silica ultimately report as reverberatory slag and the total silica additions must be made to give the most desirable final slag composition.

Ferric oxide is present in varying amounts in reverberatory slag and is in general a troublesome constituent. It tends to raise the melting point and interfere with satisfactory skimming. If ferric oxide is present in excessive amounts magnetite tends to precipitate. The sources of ferric oxide are the calcines resulting from the roasting of the concentrates and the converter slag returned to the reverberatory.

A good reverberatory slag should not be viscous and should have a relatively low specific gravity, thus allowing matte particles to settle readily before the slag is withdrawn from the furnace. These conditions are promoted by the presence or addition of small amounts of lime and alumina to the ferrous silicate. Usually there is a sufficient quantity of these oxides present in the ore-concentrate mixture or in the converter flux, but if not a small amount of limestone may be added to the reverberatory charge.

Many years of experience have determined the composition of slags which are most satisfactory in reverberatory operation. Table 6-1 shows the analyses of slags being produced at several plants; it will be noted that they are strikingly similar regardless of the fact that local plant conditions may require the production of different grades of matte.

Losses of Copper in Slags

Since refinery slags and converter slags are ultimately returned to the process, the only final loss of copper in slags is that which is carried by the discarded reverberatory slags. There are six possible forms in which the copper may exist in reverberatory slag, *viz.*, as dissolved copper silicate, dissolved copper oxide, matte particles in suspension, dissolved sulfide, dissolved copper ferrite, and dissolved metal. The extent to which the compounds are dissociated in the molten slag is unknown and our knowledge of the copper content is based almost entirely on a study of solidified slag. Published discussions differ, but the most recent studies

TABLE 6-1. ANALYSES OF COPPER REVERBERATORY SLAGS

	Composition (%)					
	SiO_2	FeO	CaO	MgO	Al_2O_3	Cu
Plant No. 1	39.0	34.7	11.0	....	7.0	0.35
Plant No. 2	38.0	45.0	7.0	....	5.0	0.40
Plant No. 3	39.0	41.1	9.0	....	6.0	0.37
Plant No. 4	40.1	33.9	7.9	....	6.9	0.42
Plant No. 5	39.7	34.2	7.9	....	7.1	0.44
Plant No. 6	34.6	41.2	8.2	....	5.2	0.51
Plant No. 7	39.8	40.5	5.1	....	8.2	0.56
Plant No. 8	34.9	47.0	4.4	....	9.4	0.55
Plant No. 9	37.6	47.6	3.2	....	6.2	0.34
Plant No. 10	32.8	52.0	3.6	....	7.1	0.54
Plant No. 11	34.0	52.6	1.1	....	6.2	0.52
Plant No. 12	38.0	47.0	1.3	....	6.2	0.36
Plant No. 13	32.5	50.0	2.3	....	7.7	0.55
Plant No. 14	36.0	48.8	1.5	2.5	....	0.42

indicate that although all the above forms are possible, nearly all the copper in the solid slag is as sulfide or ferrite. It enters the slag in four ways:

(1) In the converter slag returned to the furnace.

(2) In sulfide dissolved by the slag at the interface between the slag and matte layers.

(3) As prills of matte carried upward into the slag by gases evolved in the matte mainly from reaction between oxides and sulfides.

(4) By dust, which is continually settling on the surface of the slag.

None of these losses can be completely prevented.

Some of the copper in the converter slag is undoubtedly removed in the reverberatory, but some is not and the copper content will be kept down by avoidance of overblowing the converter. The second item is lowered by using a low smelting temperature. The third item is lowered by producing a low-grade matte and using low temperatures which tend to minimize gas-forming reactions. The fourth item is lowered by charging in such a way as to produce a minimum of dust.

Low temperatures are in general undesirable for they mean low smelting rates, which increase costs, and when all reasonable precautions are taken the reverberatory slags usually contain 0.4 to 0.5 per cent copper. This can be greatly reduced and even completely removed by fusing the slag with pyrite in a separate operation, but up to the present time the recovery of copper has not justified the cost of treatment.

Most of the copper may also be removed by granulating the slag followed by fine grinding and leaching, but this too is considered to be uneconomical.

As iron ore reserves are being depleted, the suggestion has often been made that iron be recovered from copper slags, preferably while they are still molten. This is technically possible and in fact has been done in an electric furnace, but the large amount of silica present is a hindrance to the economical operation of the process. A copper-bearing pig iron high in silicon is produced by the operation.

COPPER MATTES

Solid copper matte consists essentially of Cu_2S and FeS, each of which under normal rates of cooling contains small amounts of the other in solid solution. The equilibrium diagram of Carpenter and Hayward[9], prepared by fusing mixtures of Cu_2S and FeS and slowly cooling, is shown in Figure 6-2. This diagram is of value in showing the liquidus curves of such mixtures and the nature of the solid product, but the modern concept of the liquid is that it consists of Cu, Fe, and S, with the amount of the latter depending on its vapor pressure in the atmosphere above the charge. Some light is thrown on this by Schuhmann and Moles[10] in their paper "Sulphur Activities in Liquid Copper Sulphides." The diagram in Figure 6-2 indicates that the solidus consists of Cu_2S containing some FeS and of FeS containing some Cu_2S. This may be due to the fact that

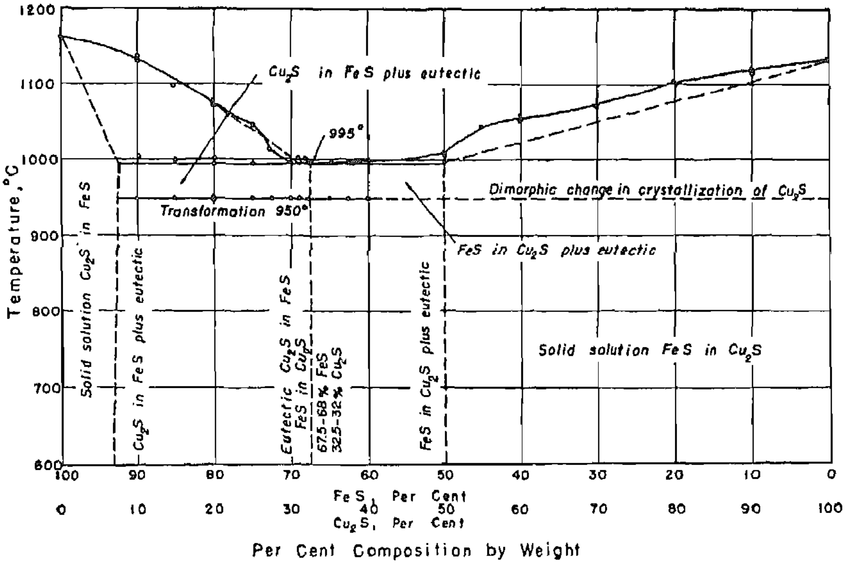

FIGURE 6-2. Phase diagram of the system Cu_2S-FeS. (*From Carpenter and Hayward.*)

the rate of cooling of the samples was too rapid to allow complete separation of the sulfides. The same type of mutual solubility is shown in the equilibrium diagram of Cu_2S-Ni_3S_2, but in a new process developed by the International Nickel Co. for the separation of nickel from copper it has been found that if the fused copper-nickel matte is poured into large blocks and cooled very slowly to well below the solidification range, the product contains the copper and nickel sulfides in distinct particles. These may be separated by flotation after crushing and grinding, yielding a copper concentrate containing only a small percentage of nickel and a nickel concentrate containing only a small percentage of copper.

In commercial mattes the copper and iron sulfides are associated with small amounts of other sulfides and also with ferric oxide and dissolved slag. The ferric oxide, which may at times be considerable in amount, distributes itself according to some as yet undetermined law between the slag and the matte. The latter being at the bottom of the furnace under a heavy layer of slag is usually at a relatively low temperature at which the reaction between the sulfide and ferric oxide does not take place. At times, however, the temperature at the slag-matte interface is sufficiently high to promote the reaction, the violence of which is a direct function of temperature.

When the temperature of the matte is low and the concentration of ferric iron in the matte high there may be a precipitation of the magnetic oxide in considerable quantities on the furnace bottom, a highly undesirable condition.

Although operating experience through the years has shown that the most desirable slag varies little from plant to plant, this is not true for matte grades, which are found to vary considerably as shown in Table 6-2.

By roasting concentrates previous to smelting, the copper metallurgist may produce almost any grade of matte he desires in the reverberatory smelting furnace. It is merely a question of how much sulfur and iron are to be oxidized in the roasting furnace and how much in the converter. The grade of matte is usually a function of the grade of concentrates not because it is necessarily so but because, for economic reasons, it is desirable. The iron which is oxidized in the roaster must be fluxed with cold silica in the reverberatory, the flux absorbing heat produced by combustion of fuel. The iron oxidized in the converter, on the other hand, furnishes sufficient heat on oxidation to produce a fused silicate from the added flux. The decision as to the relative amounts of sulfur and iron to oxidize in the roaster and the converter, or in other words the grade of matte produced, is decided in general on the above basis, but the matte grade and therefore quantity must be adjusted to the converter capacity.

TABLE 6-2. ANALYSES OF REVERBERATORY MATTES

	Composition (%)		
	Cu	Fe	S
Plant No. 1	38	25	23
Plant No. 2	43.5	27.0	25.0
Plant No. 3	39.4	32.6	22.0
Plant No. 4	39.9	23.7	24.4
Plant No. 5	39.7	24.1	23.7
Plant No. 6	48.8	20.8	25.4
Plant No. 7	33.54	34.2	26.9
Plant No. 8	33.28	34.9	26.9
Plant No. 9	32.17	35.9	27.0
Plant No. 10	34.85	35.4	24.0
Plant No. 11	34.5	36.6	25.0
Plant No. 12	24.3	43.9	23.5
Plant No. 13	44.0	28.0	25.9
Plant No. 14	38.0	31.0	25.0

This point was illustrated at a large copper plant where it was imperative to increase capacity temporarily even at some loss in efficiency. This was done by stepping up the smelting rate in the reverberatory, which at once caused overloading of the converters, but by raising the grade of matte the two operations were again brought into line.

In the smelting operations the precious metals follow the matte and finally report in the blister copper. If the second stage of the converter operation is stopped when only a small amount of blister has been made, nearly all the gold and much of the silver will be found in the metal thus produced. Advantage is sometimes taken of this fact to concentrate the precious metals in a small amount of blister copper, thus making it unnecessary to refine the remainder electrolytically for recovery of the precious metals.

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Chapter 7

Thermodynamics of Copper Smelting

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In general, the nonferrous extractive metallurgists have been rather slow in applying thermodynamic principles to the study of their processes. This is at least partly attributed to the fact that, unlike the organic chemists, the reactions with which they must deal are relatively few in number and in any given combination of reactants the possible different reactions that may take place are usually very limited. Another reason for the slowness of progress in this field may be found in the experimental difficulties involved when working at the high temperatures at which most metallurgical reactions are carried out. Moreover, while the thermodynamic approach usually results in a better understanding of processes, it does not guarantee an improvement in mode of operation or a decrease in costs—a matter of prime importance to the plant operator. In the consideration of new processes it often can predict some of the limitations involved, but because reaction rates play such an important role in determining the final outcome, experimentation is not eliminated. In spite of its limitations, however, thermodynamics is now recognized as an important tool for the extractive metallurgist, particularly for those engaged in the development of new processes.

The U.S. Bureau of Mines, under the leadership of K. K. Kelley, helped to initiate interest in metallurgical thermodynamics in the United States by its program, largely centered at its Berkeley, California, station, of compiling and determining specific heats and thermodynamic constants of metallurgical compounds[1]. That this interest is becoming more widespread is evidenced by the recent symposium of the Faraday Society on the Physical Chemistry of Process Metallurgy[2] and the program undertaken by R. Schuhmann at the Massachusetts Institute of Technology[3], the latter dealing specifically with copper smelting. Several authors have facilitated the calculations involved in metallurgical equilibria by using the best available data and calculating the free-energy change in the formation of metallurgical compounds as a function of temperature and representing them graphically. Of particular interest is the work of Ellingham[4], Richardson and Jeffries[5], Kellogg[6], and Osborn[7]. Figures 7-1 to 7-5 are taken from Osborn's paper. Here are plotted against temperature the standard free energies of formation associated with the utilization of one gram-mole of the combining gas. Oxides, sulfides, chlorides, sulfates, and carbonates are considered, and in each instance the free-energy change is that corresponding with the

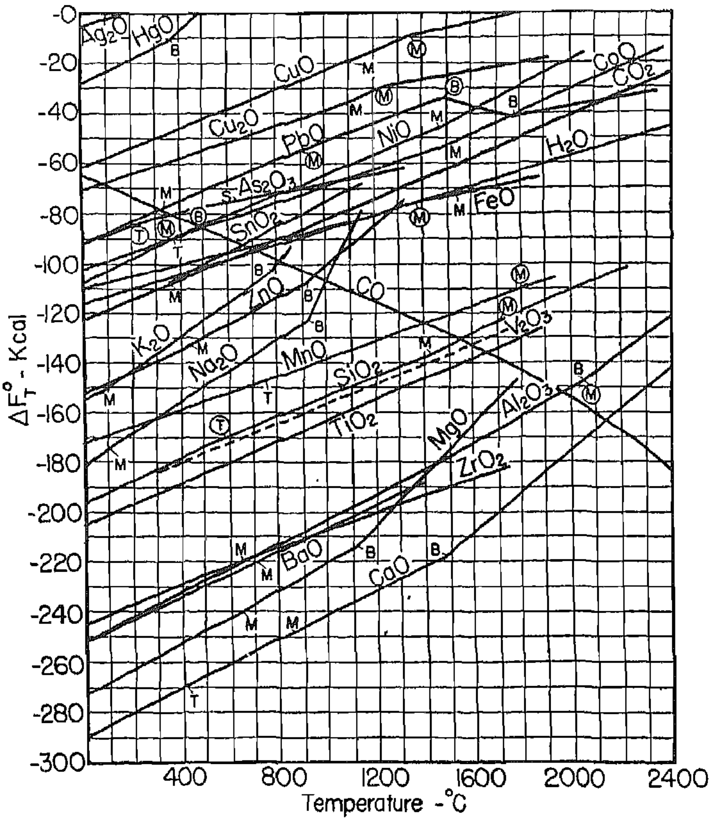

FIGURE 7-1. The standard free energies of formation of oxides per gram-mole of oxygen as a function of temperature. Legend for this and subsequent figures:

M: melting point of the metal or starting oxide
Ⓜ: melting point of the product
B: boiling point of the metal or starting oxide
Ⓑ: boiling point of the product.
T and Ⓣ: transition points.
(*Courtesy of Journal of Metals.*)

reaction of one gram-mole of the gas—O_2, S_2, Cl_2, SO_3, and CO_2, respectively—with the corresponding stoichiometric amounts of the metal or oxide.

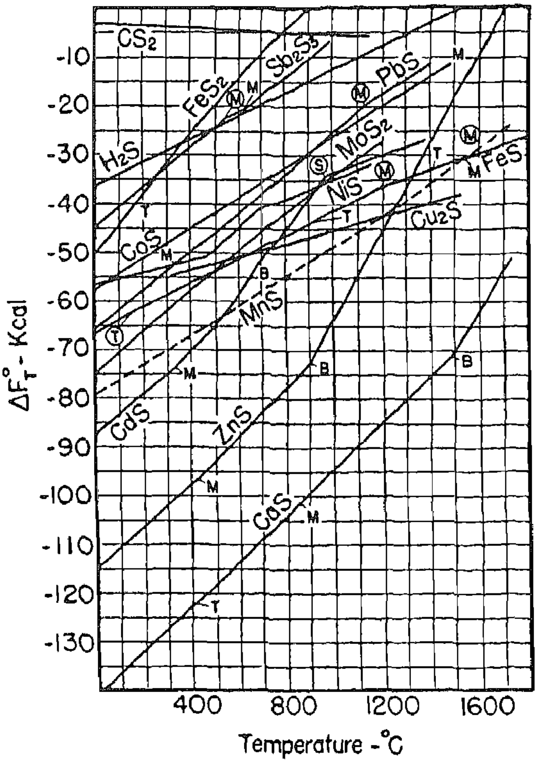

FIGURE 7-2. The standard free energies of formation of sulfides per gram-mole of sulfur (S_2) as a function of temperature. (The values for FeS_2 are for 2FeS and S_2.) (*Courtesy of Journal of Metals.*)

In these graphs the use of one gram-mole of gas as the basis for the computations makes possible the direct comparison of the relative "affinities" of the metals or oxides for the gases. The more stable compounds appear at the bottom of the graphs and the least stable ones at the top. At a given temperature a metal is able to displace from their compounds all other metals that appear above it on the respective figures, provided all reactants and products are in their standard states. The fact that on most of the graphs many of the curves cross each other points out that the relative stability changes with temperature. By the proper combination of the reactions represented by these graphs, the

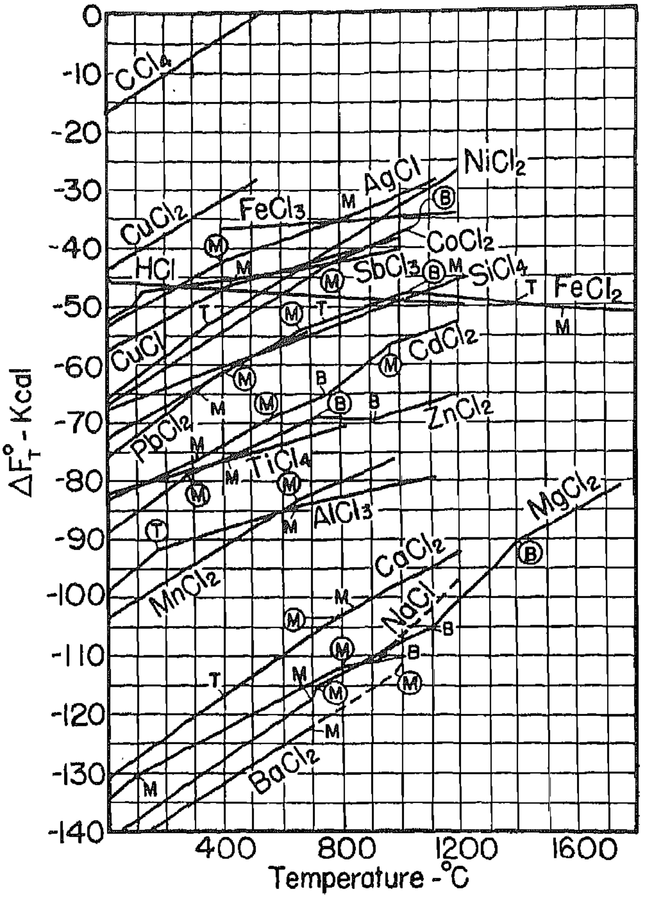

FIGURE 7-3. The standard free energies of formation of chlorides per gram-mole of chlorine as a function of temperature. (*Courtesy of Journal of Metals.*)

free-energy change for a wide variety of reactions can be obtained relatively quickly without tedious calculations.

The free-energy changes given (ΔF°) are for reactants and products in their standard states, a situation which usually does not prevail in most reactions of practical interest. The free-energy change (ΔF) is obtained in these cases by adding to the standard free-energy change a term $RT\ln a$. For the general reaction:

$$bB + cC = dD + eE \tag{1}$$

$$\Delta F = \Delta F^\circ + RT\ln \frac{A_D{}^d \cdot A_E{}^e}{A_B{}^b \cdot A_C{}^c} \tag{2}$$

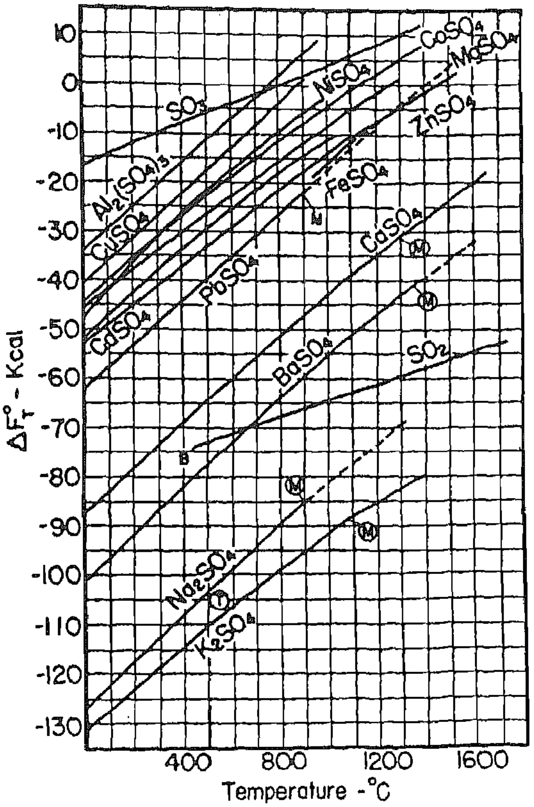

FIGURE 7-4. The standard free energies of formation of sulfates per gram-mole of SO_3 as a function of temperature. (*Courtesy of Journal of Metals.*)

where A = activity of a constituent

T = absolute temperature, degrees Kelvin

R = gas constant

$$a = \frac{A_D{}^d \cdot A_E{}^e}{A_B{}^b \cdot A_C{}^c}$$

If the activity values are known, the free-energy changes accompanying reactions with reactants and products at other than standard states can readily be obtained by combining the ΔF° values from the graphs with equation (2).

Copper smelting will be considered here in the broad sense, that is, roasting, smelting, converting, and furnace refining. These are the unit operations usually carried out in a copper smelter, and in the case where direct matte smelting is employed without roasting, the minerals undergo reactions similar to those taking place in the roasters.

Roasting

The sulfide minerals most commonly present in copper ores or concentrates to be roasted are chalcocite (Cu_2S), covellite (CuS), chalcopyrite ($CuFeS_2$), and pyrite (FeS_2). We shall, therefore, turn our attention to reactions involving these compounds.

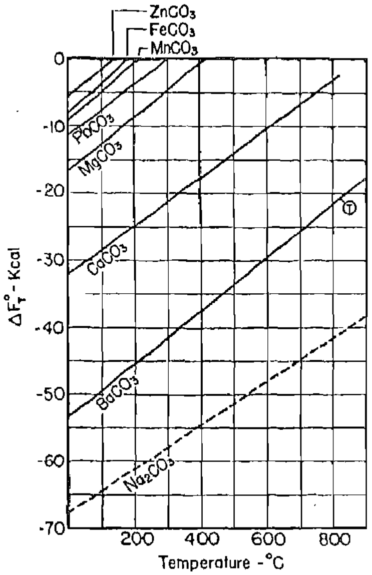

Figure 7-5. The standard free energies of formation of carbonates per gram-mole of CO_2 as a function of temperature. (*Courtesy of Journal of Metals.*)

Covellite, pyrite, and chalcopyrite undergo pyritic sublimation, and because partial roasting is practiced, the new phases formed may be involved in formation of matte in the subsequent operation. The sublimation reactions, according to the latest researches[8], are:

$$9CuS(s) \rightleftharpoons Cu_9S_5(s) + \frac{4S_x}{x}(g) \qquad (3)$$

$$FeS_2(s) \rightleftharpoons FeS_{1.18}(s) + \frac{0.82S_x}{x}(g) \qquad (4)$$

$$2CuFeS_2(s) \rightleftharpoons Cu_2S(s) + 2FeS(s) + \frac{1S_x}{x}(g) \qquad (5)$$

The rate of sublimation and the sulfur vapor pressures generated are quite high at relatively low temperatures. The decomposition is materially aided in roasting because of the removal of the sulfur by combination with the oxygen of the atmosphere:

$$\tfrac{1}{2}S_2(g) + O_2 = SO_2(g) \tag{6}$$

$$SO_2(g) + \tfrac{1}{2}O_2 \rightleftharpoons SO_3(g) \tag{7}$$

As a result, the sulfate or oxide phases are formed by reaction of the oxygen with the solid product of sublimation, *i.e.*, Cu_9S_5, $FeS_{1.18}$, and Cu_2S, respectively, and in the case of chalcocite, by reaction with the mineral. Peretti[9] has shown that the pertinent reactions with Cu_2S are:

$$Cu_2S(s) + 1\tfrac{1}{2}O_2 = Cu_2O(s) + SO_2(g) \tag{8}$$

$$Cu_2O(s) + \tfrac{1}{2}O_2 \rightleftharpoons 2CuO(s) \tag{9}$$

$$2CuO(s) + SO_3(g) \rightleftharpoons CuSO_4.CuO(s) \tag{10}$$

$$CuSO_4.CuO(s) + SO_3(g) \rightleftharpoons 2CuSO_4(s) \tag{11}$$

The free-energy values plotted in Figures 7-1 and 7-2 show that at roasting temperatures reactions (6) and (8) and corresponding ones involving the iron compounds exhibit such large free-energy changes that the equilibrium SO_2/O_2 ratios need not be considered. However, the thermodynamics of (7), (9), (10), and (11) are such that the temperature and partial pressure of sulfur trioxide or oxygen determine which of the solid phases are stable.

The equilibrium constants are:

$$K_7 = \frac{p_{SO_3}}{p_{SO_2} \times \sqrt{p_{O_2}}} \tag{12}$$

$$K_9 = \frac{1}{\sqrt{p_{O_2}}} \tag{13}$$

$$K_{10} = \frac{1}{p_{SO_3}} \tag{14}$$

$$K_{11} = \frac{1}{p_{SO_3}} \tag{15}$$

According to the phase rule a system in which SO_2, O_2, SO_3, CuO, Cu_2O, $CuSO_4.CuO$, and $CuSO_4$ are in equilibrium is nonvariant, and this will be at the point where

$$p_{SO_3} = \frac{1}{K_{11}} = \frac{1}{K_{10}} = \frac{K_7}{K_9} p_{SO_2} \tag{16}$$

For the coexistence of gas (SO_2, O_2, SO_3) and CuO, $CuSO_4.CuO$, and $CuSO_4$ the system is univariant.

$CuSO_4$ alone will be the stable solid phase at a given temperature, if

$$P_{SO_3} > \frac{1}{K_{11}} \text{ and } \frac{1}{K_{10}}$$

CuO will exist as the sole stable solid phase if $P_{SO_3} < \frac{1}{K_{10}}$, while the intermediate phase $CuSO_4.CuO$ can thermodynamically exist alone with gas if $P_{SO_3} < \frac{1}{K_{11}}$ and $> \frac{1}{K_{10}}$.

It is obvious, however, that if the roasting be carried out under nonequilibrium conditions, the solid phases present in the calcine may be determined largely by the relative rates of the reactions involved.

Matte Smelting

If direct smelting of concentrates is practiced, the reactions undergone by the sulfide minerals in the matte furnace may be the same as those described in the preceding section. The degree to which this is true will be governed to a great extent by the rate at which the charge is melted down. In any event some sulfur elimination takes place, and eventually two liquid phases are formed in the reverberatory furnace—matte (the sulfur-rich phase) and slag (the silicate-rich phase). As reaction between the two liquids can proceed at the liquid-liquid interface, the ultimate composition of matte and slag may approach thermodynamic equilibrium.

A commercially produced matte is a complex system containing chiefly iron, copper, sulfur, oxygen, silicon, and the precious metals, and very little experimental work has been carried out to determine the thermodynamic relationships existing between the various components. However, considerable is known regarding the simplified ternary system copper-iron-sulfur showing the freezing points and composition ranges of artificial mattes. Figure 7-6 is taken from a paper by Peyronel and Pacilli[10] and coordinates their work with the previous researches of Guertler-Reuleaux, Bornemann-Schad, and Merwin-Lombard. In Figure 7-6, the matte compositions of practical importance lie in the region below a straight line drawn through Cu_2S and FeS because liquid mattes whose compositions lie on this line develop a sulfur partial pressure which is a substantial fraction of an atmosphere. Therefore, unless the escape of sulfur vapor is prevented, the composition changes to some value having a lower sulfur pressure, *i.e.*, toward the Fe-Cu side of the diagram. Here, however, a miscibility gap is encountered (two liquid phases in equilibrium), and commercial mattes will fall in the narrow

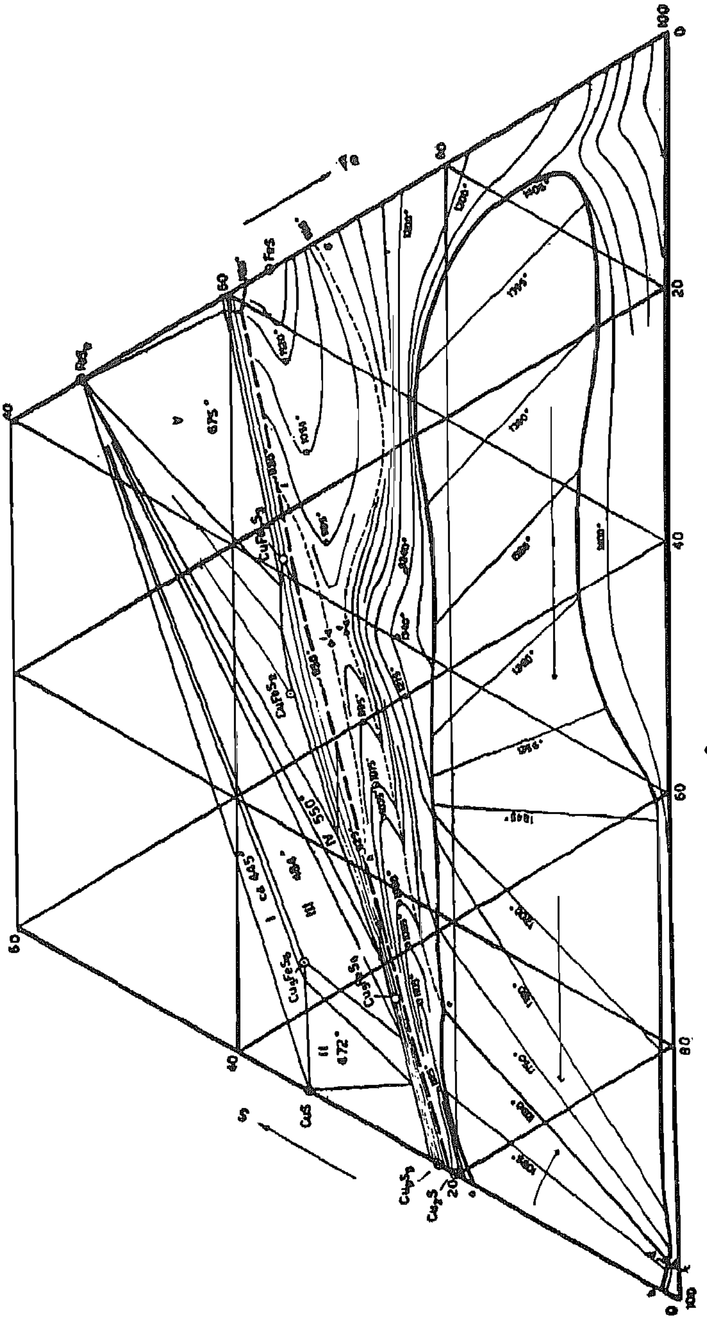

FIGURE 7-6. A portion of the ternary system copper-iron-sulfur. (*After Peyronel and Pacilli.*)

region bounded by the miscibility gap line and a line joining Cu_2S and FeS.

No determinations have been made of sulfur pressures in the ternary system Cu-Fe-S at copper smelting temperatures, but Cox and coworkers[11] and Schuhmann and Moles[12] have done so for liquid copper sulfide. The latter have determined that

$$\log P_{S_2} = \frac{-15{,}505}{T} + 4.56 \tag{17}$$

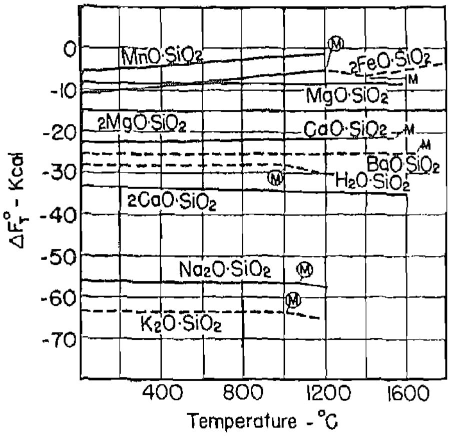

FIGURE 7-7. The standard free energies of formation of silicates per gram-mole of SiO_2 *as a function of temperature.* (*Courtesy of Journal of Metals.*)

expresses the sulfur pressure for a system containing two conjugate solutions, liquid Cu_2S and liquid Cu.

Little is known directly of the free energies of formation of slag systems, but Richardson[5] has collected the data for those silicates for which reliable data exist and these are shown in Figure 7-7. Schuhmann[13] has proposed a qualitative ternary SiO_2-Fe_2O_3-FeO diagram based on the known FeO-SiO_2 binary and Darken's Fe-O diagram. By the use of Darken's[14] data Schuhmann has constructed Figure 7-8 for iron silicate slags at 1300°C. The outstanding feature shown by this figure is the large difference in oxygen pressure for slags in equilibrium with metallic iron and those in equilibrium with magnetite—a range of variation in the pressure of oxygen of about 10^6-fold. Employing activities of FeO given in Figure 7-8 for the reaction (any other reactions involving SO_2 could be used equally well):

$$3Fe_3O_4(s) + FeS(l) \rightleftharpoons 10FeO(l) + SO_2(g) \tag{18}$$

Schuhmann has calculated the extreme limits of SO_2 pressures for the

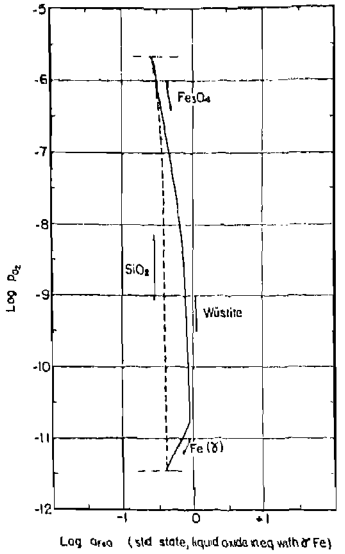

FIGURE 7-8. Activities of FeO and O_2 in iron silicate melts at 1300°C. (*After Schuhmann.*)

matte-smelting step. The equilibrium constants are 10^{-4}, 4.9×10^{-3}, and 1.5×10^{-1} at 1200, 1300, and 1400°, respectively, and

$$K_T = \frac{P_{SO_2} \times (A_{FeO})^{10}}{(A_{FeS})\ (A_{Fe_3O_4})^3} \tag{19}$$

$$P_{SO_2} = \frac{K_T\ (A_{Fe_3O_4})^3 \times (A_{FeS})}{(A_{FeO})^{10}} \tag{20}$$

For a given matte composition the SO_2 pressure will be at a maximum when the ratio

$$(A_{Fe_3O_4})^3 \ / \ (A_{FeO})^{10}$$

is greatest, a condition that exists when the slag is saturated with magnetite and silica because $A_{Fe_3O_4}$ will be unity and $A_{FeO} = 0.28$ (Figure 7-8) at 1300°C. At 1200 and 1400°C., $A_{FeO} = 0.29$ and 0.18, respectively. Substituting these values in equation (20) for a 30 per cent Cu matte ($A_{FeS} = 0.75$) yields the following values for the maximum SO_2 pressure: 17 atm. at 1200°C, 21×10^2 atm. at 1300°C, and 25×10^5 atm. at 1400°C.

The minimum SO_2 pressures will be obtained with a slag saturated with metallic iron and silica. By calculating the proper activities for FeO and Fe_3O_4 from Darken's data, the minimum SO_2 pressures for the

30 per cent Cu matte are: 6.5×10^{-7} atm., 2×10^{-6} atm., and 4.9×10^{-6} atm. at 1200°C, 1300°C, and 1400°C, respectively. From equation (20) it is apparent that as the matte grade is increased the SO_2 pressure is decreased. It can be concluded, then, that for a given grade of matte the equilibrium SO_2 pressure can be varied enormously by changing the slag composition.

Kelley and Schuhmann both have shown the strong tendency for copper sulfide formation in the matte furnace by the following reaction:

$$Cu_2O(l) + FeS(l) \rightleftharpoons Cu_2S(l) + FeO(l) \qquad (21)$$

For this reaction at 1300°C,

$$K = \frac{A_{Cu_2S} \times A_{FeO}}{A_{FeS} \times A_{Cu_2O}} = 4 \times 10^3 \qquad (22)$$

If the activities of Cu_2S and FeS are approximately equal and the FeO activities from Figure 7-8 prevail, the activity of the Cu_2O is found from equation (22) to be about 10^{-4}. This accounts in no small measure for the concentration of the copper into the matte and the iron into the slag.

Converting

During the slag-forming period in the converting of copper mattes, slag is formed by reaction of the siliceous flux added with the iron oxides formed by the blowing operation. The mechanism is not known, but the thermodynamic situation can be assessed by the use of the following equations:

$$FeS(l) + 1\tfrac{1}{2}O_2(g) = FeO(l) + SO_2(g) \qquad (23)$$

$$FeS(l) + \tfrac{1}{2}O_2(g) \rightleftharpoons FeO(l) + \tfrac{1}{2}S_2(g) \qquad (24)$$

$$Cu_2S(l) + 1\tfrac{1}{2}O_2(g) = Cu_2O(l) + SO_2(g) \qquad (25)$$

$$Cu_2O(l) + FeS(l) \rightleftharpoons FeO(l) + Cu_2S(l) \qquad (21)$$

The incoming oxygen probably forms FeO (also Fe_2O_3 and Fe_3O_4) and Cu_2O, but as has been pointed out in the preceding section, the thermodynamic relationships of equation (21) are such that very little Cu_2O is stable in a matte containing FeS. This explains the well-known result achieved in practice, namely, the elimination chiefly of iron (and sulfur) from the matte.

Kelley[15] has calculated thermodynamically the possibility of obtaining elemental sulfur from the copper converter and has concluded that the theoretical recovery increases with increasing temperature. At 1600°K it should be possible, if operating under equilibrium conditions, to recover 16 per cent of the sulfur and at 2000°K, the recovery is theoretically 50 per cent.

In the second stage of blowing, if we simplify matters by considering "white metal" to be Cu_2S, the copper-sulfur diagram, Figure 7-9, is of interest. Peretti[16] has pointed out that the blowing is carried out with only one liquid in the vessel, a sulfur-rich phase, for approximately 14 per cent of the blowing time. This is followed by a long period (75 per cent of the total time) when two liquids of unchanging composition are present (*c* and *b* in Figure 7-9). In a side-blown converter it can be arranged to blow into the sulfur-rich phase only, as shown in Figure 7-10. Finally the sulfur-rich phase disappears completely, and only one liquid phase is again present to the end of the blow. The relative densities of the two liquid phases are such that the copper-rich phase is found at the bottom of the converter. This condition, plus the fact that the rate of heat evolution through oxidation of the copper-rich phase is probably low, leads to a freeze-up when bottom blowing is practiced. From a thermodynamic consideration alone bottom blowing is feasible.

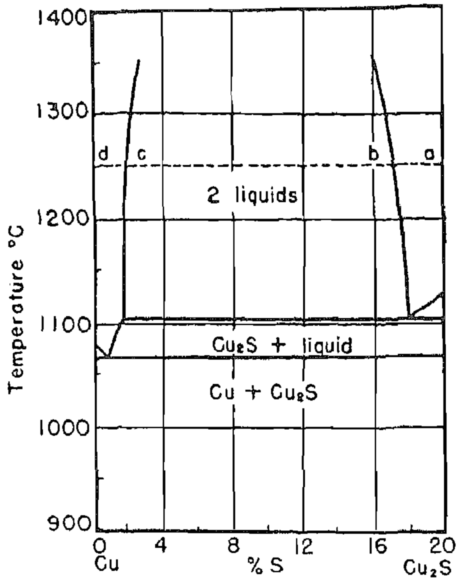

FIGURE 7-9. A portion of the Cu-S phase diagram.

Fire Refining

Of great importance in the fire-refining step is the solubility of gases in the molten copper. Because refining is accomplished by over-oxidation followed by reduction (poling) in a fuel-fired furnace whose products of combustion are in contact with the liquid metal, the gases of greatest importance are oxygen, hydrogen, carbon dioxide, and sulfur dioxide.

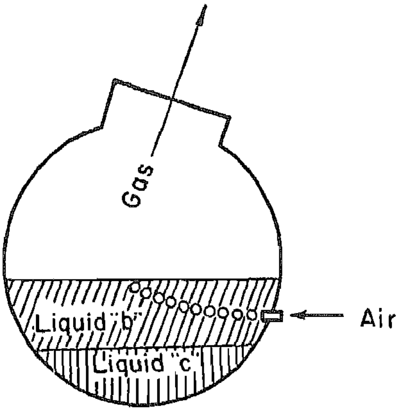

FIGURE 7-10. Blowing into the sulfur-rich phase in the copper converter.

An excellent discourse on this topic was given by A. J. Phillips[17]. Using the thermodynamic data determined by Floe and Chipman[18] for the reaction

$$6Cu(l) + SO_2(g) \leftrightharpoons Cu_2S \text{ (in liq. Cu)} + 2Cu_2O \text{ (in liq. Cu)}, \qquad (26)$$

Phillips constructed Figure 7-11, showing the sulfur and oxygen contents of copper in equilibrium with various partial pressures of SO_2 at 1250°C.

The equilibrium constant, K, is expressed as:

$$\frac{[S] \times [O]^2}{P_{SO_2}} \qquad (27)$$

Chipman and Floe's values for K at 1083 and 1250°C are 0.98×10^{-5} and 3.31×10^{-5}, respectively. From this Phillips concludes that there is no commercial fuel low enough in sulfur to permit its use in retaining molten copper "at set" for an indefinite period of time, since properly prepared copper will contain less than 0.03 per cent oxygen, and the sulfur content must not exceed 0.002 per cent. Figure 7-12 shows the calculated oxygen and sulfur concentrations necessary to produce SO_2 bubbles in copper at 1083°C at one atmosphere pressure. At least 0.04 per cent S in the liquid metal is necessary for SO_2 alone to separate.

If the oxygen content of the molten metal is less than the eutectic composition, an increased concentration of sulfur must be present for SO_2 separation. One also gathers from the graph that no SO_2 bubble evolution is possible if the oxygen content is less than 0.1 per cent, even if the sulfur content is increased to 0.77 per cent, the sulfide eutectic composition.

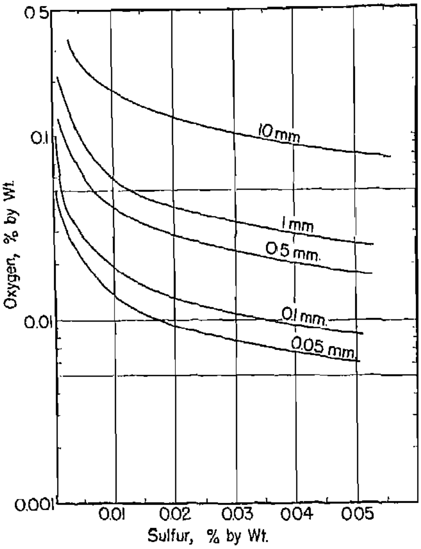

FIGURE 7-11. The sulfur and oxygen contents of liquid copper at 1250°C in equilibrium with SO_2 at various pressures. *(After Phillips.)*

By considering equilibrium in the following reaction at 1083°C

$$Cu(l) + H_2O(g) \rightleftharpoons Cu_2O \text{ (in liq. Cu)} + H_2(g), \qquad (28)$$

Phillips[19] showed the effect of freezing upon the theoretical oxygen and hydrogen contents of liquid copper. For a copper melted and heated in

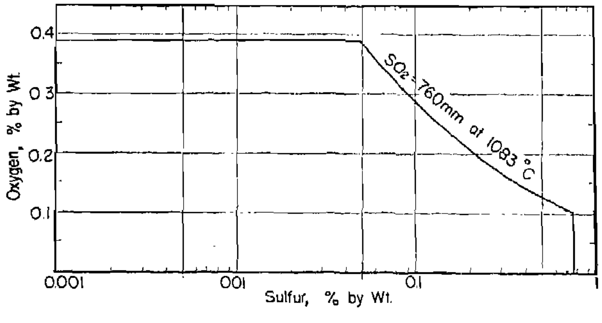

FIGURE 7-12. SO_2 equilibrium with molten copper at the melting point, 1083°C. *(After Phillips.)*

an oxidizing atmosphere to 1250°C and poled to 0.015 per cent oxygen, the hydrogen content should not be more than 5×10^{-5} per cent. As freezing takes place the composition of the solid approaches 1.8×10^{-5} per cent hydrogen and 0.00075 per cent oxygen, and the liquid will contain 5.2×10^{-5} per cent hydrogen and 0.026 per cent oxygen when $H_2O + H_2$ gas will be evolved. As freezing progresses the oxygen content of the liquid will increase and the hydrogen content will decrease. About 15 per cent gas by volume will be evolved. In order to prevent gas separation from this metal during freezing, the oxygen content must be lowered to 0.000085 per cent unless the metal is deoxidized with a residual deoxidizer such as phosphorus.

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Chapter 8

Electrolytic Copper Refining

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The first patents on electrolytic refining of copper were those of James Elkington, published in England in 1865-1870. The first electrolytic copper refinery in the United States, built in Newark, New Jersey, by the Balbach Smelting and Refining Company, was operated from 1883 to 1918.

The early electrolytic refiners had trouble producing firm cathode deposits of high-purity copper[1]. The use of addition agents, particularly salt, and improvements in the circulation and content of the electrolyte were the most important developments in overcoming the early difficulties. After the electrolytic refiners were regularly producing a product of higher purity and conductivity than Lake copper, it took a long time for the consumers to give recognition to this fact. One of the oldest brands of electrolytic copper that is still being produced is L.N.S., or Nichols Lake Substitute. The name indicates the early conception of electrolytic copper as a product. Electrolytic copper became the official basis for price quotations in 1914.

In 1927, S. Skowronski[2] reviewed the progress made in the electrolytic refining of copper. He stated: "Electrolytic refining of copper may be considered the pioneer of our electrochemical industry of today, and the basic principles and theories underlying the practice were well understood in 1902. Consequently, no radical change involving the theories has taken place within the last twenty-five years. In order to handle the increased production, the individual operations and units have all had to be enlarged and mechanical appliances installed to replace hand labor." With some qualification, the same statement is valid today after elapse of another twenty-five years.

There has been a decrease, rather than an increase, in the rated capacity of the refineries that existed in 1927, but two new refineries have been placed in operation. The major improvements have been in type and layout of equipment, and materials of construction.

A tabulation[2] of the capacity of the electrolytic copper refineries operating in the United States in 1927 indicates a total rated production of 1,444,000 short tons per year as compared with 339,450 tons in 1902. The following tabulation shows the comparative rated capacities for 1927 and 1952:

	Short Tons per Year	
	1927	1952
American Smelting & Refining Co., Baltimore, Md.	360,000	198,000
American Smelting & Refining Co., Barber, N. J.	120,000	168,000
American Smelting & Refining Co., Tacoma, Wash.	102,000	120,000
Anaconda Copper Mining Company, Great Falls, Mont.	162,000	150,000
International Smelting & Refining Co., Perth Amboy, N. J.	270,000	240,000
Kennecott Copper Corporation, Garfield, Utah	....	144,000
Phelps Dodge Refining Corporation, El Paso, Texas	....	240,000
Phelps Dodge Refining Corporation, Laurel Hill, N. Y.	250,000	144,000
U. S. Metals Refining Company, Carteret, N. J.	180,000	160,000
Totals	1,444,000	1,564,000

Note: The above figures do not include production from electrowinning processes.

Refineries in Canada, Spain, Belgium, Australia, and Japan were cited with a total production capacity of 238,000 tons per year in 1927[2]. This does not include the production from small refineries located in England, Australia, and Germany, or the copper from the electrowinning processes operating in Africa or Chile. By the end of 1952, the total potential production from electrolytic refineries operating outside of the United States, but not including U.S.S.R., was approximately 940,000 tons per year. The two largest of these are located in Canada. The Montreal East Refinery of Canadian Copper Refiners Limited has a rated capacity of 135,000 tons, and the Copper Cliff Refinery of The International Nickel Company of Canada, Ltd., has a rated capacity of 168,000 tons.

Altogether there are 20 major copper refineries in the world, outside U.S.S.R. Recently completed is the Mufulira Refinery in Northern Rhodesia.

Application

In the electrolytic refining of copper the time interval, from the charging of blister or scrap copper into the anode furnace to the casting of refined shapes from the wirebar furnace, is from 22 to 37 days. The major portion of this period is in the electrolytic process of converting anode copper into cathode copper.

In fire refining of copper, the total refining period is only from 24 to 48 hours. If the products were comparable, electrolytic refining would not exist. Fire refining is employed in the production of Lake copper. In this case, silver and arsenic, the principal impurities in the ore from which Lake copper is produced, impart special properties to the final product. Lake copper has specifications separate from those for electrolytic copper. Where the blister treated is unusually low in impurities and precious metals, fire refining is employed. However, except in few instances, and then not consistently, the product will not qualify under the A.S.T.M. specification for electrolytic tough-pitch copper. This specification requires a minimum conductivity of 100 per cent, and copper plus silver content of at least 99.90 per cent. Furthermore, this specification is not the final criterion. To meet competition and to satisfy the requirements of the fabricators and the electrical industry, the electrolytic refinery must supply a product of 99.95 to 99.96 per cent minimum copper content, 101 per cent minimum conductivity, and not over 0.5 oz per ton silver. The total metallic impurities in electrolytic tough-pitch wirebar and ingots is invariably less than 0.01 per cent.

Most copper ores carry appreciable amounts of silver and gold, and frequently traces of platinum and palladium. These metals follow copper through the smelting operations and are recovered in the final smelter product, blister copper. The byproduct recovery of precious metals from the electrolytic refining of copper is a major source of these metals. The only economic method known for separating the precious metals from the blister copper is electrolytic refining. This process concentrates the precious metals in the anode slime, and so effectively that their economic recovery is possible. The treatment of electrolytic copper refinery slime is described in Chapter 11.

The Process and Basic Theory (Behavior of Copper)

The economic feasibility of electrolytic copper refining is based on the following facts. Copper can be separated from the other metals and impurities by electrolysis in a bath (electrolyte) which is basically a solution of copper sulfate and sulfuric acid. This bath is relatively simple and inexpensive to maintain. Copper is sufficiently electropositive to hydrogen in this solution to facilitate its deposition at relatively high current efficiency without delicate adjustments. Relatively wide variations in content and temperature of the electrolyte and of current density can be employed with satisfactory results. The metallic inpurities more noble (electropositive) than copper do not tend to enter the electrolyte at current densities that can be employed economically. The metals that do enter the electrolyte, along with copper, are either precipitated as insoluble compounds, or being less noble than copper, remain in solution but do not deposit electrolytically at the cathode. Procedures necessary to prevent their accumulation in the electrolyte are normally not excessively complicated or costly.

Under the conditions that obtain in commercial refining practice, copper is dissolved from the anode and enters the electrolyte almost entirely through the process of electrolytic oxidation. At the cathode the deposition of copper is accomplished by electrolytic reduction. Considering that the reactions are entirely in accord with the behavior of copper as a bivalent metal, they can be expressed as follows:

$$\text{Anode:}\quad Cu - 2e \rightarrow Cu^{++} \tag{1}$$

$$\text{Cathode:}\quad Cu^{++} + 2e \rightarrow Cu \tag{2}$$

In accord with the theory of Luther, Allmand[3] shows that the preceding reactions may partially occur in two steps:

$$\text{Anode:}\quad Cu - e \rightarrow Cu^{+} \tag{3}$$

$$Cu^{+} - e \rightarrow Cu^{++} \tag{4}$$

$$\text{Cathode:}\quad Cu^{++} + e \rightarrow Cu^{+} \tag{5}$$

$$Cu^{+} + e \rightarrow Cu \tag{6}$$

The conception of the reaction as occurring in two steps[4] offers a basis for one explanation of the fact that in actual plant operations neither the amount of copper entering the solution or deposited therefrom is entirely in accord with its behavior as a bivalent metal. There are several explanations of this fact, all of which will be discussed under the subject of current efficiency.

Cu_2O is present in the anode in amounts of 0.5 to 3.0 per cent. This reacts directly with H_2SO_4 in the electrolyte:

$$Cu_2O + H_2SO_4 \rightarrow CuSO_4 + H_2O + Cu\downarrow \tag{7}$$

Thus, half of the copper in the Cu_2O enters the solution by chemical reaction and half is precipitated in the form of very fine metallic particles. The latter may enter the slime which accumulates in the bottom of the cell, or if reoxidized, they react with H_2SO_4 to form $CuSO_4$.

Oxygen is only slightly soluble in the electrolyte, but occurs in concentrations sufficient to take part in some reactions to be described later. It may oxidize Cu^{+} ion to Cu^{++} ion or directly oxidize copper in the anode or cathode. Either reaction would result in an increase in anode current efficiency or a decrease in cathode current efficiency or both.

$$2Cu^+ + \tfrac{1}{2}O_2 + 2H^+ \rightarrow 2Cu^{++} + H_2O \qquad (8)$$

or

$$Cu + \tfrac{1}{2}O_2 + H_2SO_4 \rightarrow CuSO_4 + H_2O \text{ and } CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$$

which essentially amounts to

$$Cu + \tfrac{1}{2}O_2 + 2H^+ \rightarrow Cu^{++} + H_2O \qquad (9)$$

There is contrary evidence in regard to the ability of Fe^{+++} ion to oxidize metallic copper or Cu^+ ion when operations are conducted with copper anodes and with the iron content of the electrolyte within the limits of normal refining practice. If it does, the reactions and results would be similar to those involving oxidation by oxygen.

Chlorine is added to the electrolyte in the form of NaCl or HCl. The amount is relatively small and the addition is for the purpose of precipitating silver and improving the structure of the copper deposit. Some chlorine may react with Cu^+ ion with the result that cuprous chloride, Cu_2Cl_2 is precipitated:

$$2Cu^+ + 2Cl^- \rightarrow Cu_2Cl_2\downarrow \qquad (10)$$

As will be shown later, some copper is present in the anode in the form of sulfides, selenides, and tellurides, which are chemically and electrochemically insoluble. These compounds enter the slime and the combined copper does not enter the electrolyte.

Detailed descriptions of the behavior of copper and the accompanying impurities are abundant[5].

Behavior of Silver, Gold, Platinum, Palladium, Sulfur, Selenium, and Tellurium

Silver, gold, platinum and palladium are more electropositive than copper and, hence, could be deposited at the cathode if they entered the electrolyte even in small amounts. Of these, probably only silver is dissolved anodically and this only to a slight extent. Silver entering the electrolyte would be precipitated as silver chloride by the chlorine present, but evidence is lacking to prove whether or not the precipitation is complete. As the anode is corroded away, the gold, platinum, palladium, and practically all of the silver remain insoluble, and along with other impurities, form what is called anode slime or anode mud. For the most part, this slime settles out of the electrolyte and accumulates at the bottom of the cells. The fact that silver and gold are found in cathodes is due chiefly, if not entirely, to the fact that a small portion of the slime becomes occluded in the cathode deposit. All the other ingredients of the slime are also found in the deposit and some of the impurities in the cathodes could not have been deposited by electrochemical reactions.

Considering silver and gold in the cathodes as metal losses, the following generalities may be stated. The total loss of silver and gold in the cathodes increases with increase in the concentration of silver and gold in the anodes. However, the percentage loss of either metal decreases with increase of concentration in the anode. In most cases the percentage loss of silver is slightly higher than that of gold.

The evidence in regard to the relationship between silver and gold losses and current density is conflicting. In some cases refineries find a definite tendency for the losses to increase with the current density. In other cases the relationship between the losses and current density is reported as inconsistent. Generally, the difficulty of producing smooth and dense copper deposits increases with the current density and the silver and gold losses reflect the character of the deposit. The losses increase with decrease in distance between electrodes. For silver loss relationships, see Figure 8-1.

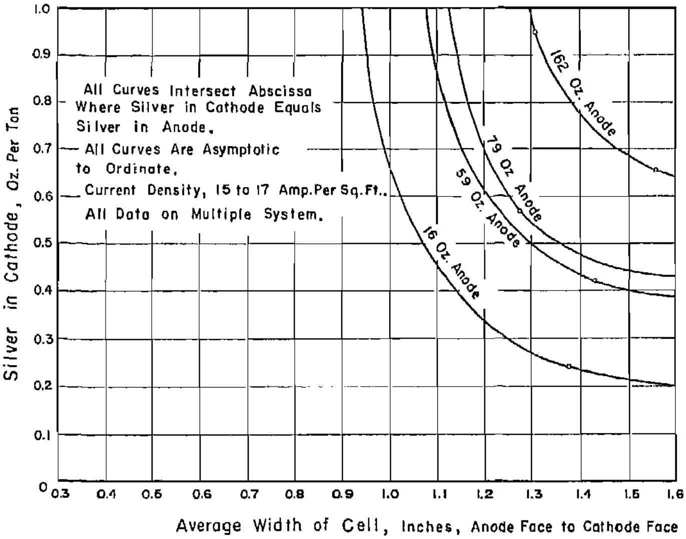

FIGURE 8-1. Relation of the silver content of the cathode to the silver content of the anode and width of cell. (H. H. Stout).

The amount and composition of the anode slime probably have an important bearing on the losses, since both of these factors influence the settling rate, which in turn affects cathode contamination.

Selenium, tellurium, and sulfur are present in the anodes as Ag_2Se, Cu_2Se, Ag_2Te, and Cu_2S. All of these substances are insoluble in the electrolyte and enter the anode slime. Selenium and tellurium in the anodes[6] combine first with silver. The excess, if any, above the silver equivalent combines with copper. Thus the amounts of selenium, tellurium, and sulfur in the anode influence the amount of copper in the slime. A selenium percentage of 0.01 is equivalent to approximately 7.97 oz per ton of silver, or 0.016 per cent copper; 0.01 per cent tellurium is equivalent to approximately 4.93 oz per ton of silver or 0.012 per cent copper; 0.01 per cent sulfur is equivalent to 0.04 per cent copper. From the data in Table 8-3 it appears that, in the majority of the refineries, the silver goes into the slime entirely as Ag_2Se or Ag_2Te and that some copper is precipitated as Cu_2Se.

Behavior of Arsenic, Antimony, and Bismuth

In the electromotive series, arsenic, antimony, and bismuth are placed between copper and hydrogen. At low copper concentrations it is possible to codeposit these metals with copper. Fortunately, the content of bismuth is very low in most blister copper and the solubilities of both antimony and bismuth are limited in normal tank-room electrolytes, antimony being soluble to a maximum of approximately 1.1 grams per liter, and bismuth to approximately 1.8 grams per liter. Arsenic is quite soluble in commercial electrolyte and has the most positive electrode potential of the three metals.

Under conditions that exist in electrolytic copper refining, the copper content of the electrolyte rather than the content of arsenic, antimony, or bismuth is the major factor in determining the electrolytic deposition of these metals on the cathode. Were arsenic deposited at its theoretical electrode potential, and there is considerable evidence in support of the fact that it is not, the copper content of the electrolyte would have to drop to approximately 18 grams per liter before the codeposition of arsenic began. This assumes an electrolyte temperature of over 50°C and current density up to 25 amperes per sq ft. Under these conditions, it is estimated that the electrolytic deposition of any of the three metals does not occur until the copper content of the electrolyte has dropped to less than 10 grams per liter. This estimate is based on the cathode potential and results obtained in the operation of liberator tanks where the copper is plated out with the use of insoluble anodes. In these tanks, the liberation or deposition of hydrogen, arsenic, and antimony appears to commence at about the same copper content, which is between 5 and 10 grams of copper per liter. Faulty circulation may result in local depletions of the copper content of the electrolyte to the point where arsenic or antimony may be codeposited with copper when the average copper content of the electrolyte is above the critical point. However, the copper content of normal tank-room electrolyte provides a considerable margin of safety.

Skowronski[7] presents experimental data proving that arsenic is not electrodeposited along with copper in proportion to the arsenic content of the electrolyte and states that with normal current density and copper content of the electrolyte, 60 grams of arsenic per liter in the electrolyte will not necessarily cause a serious deposit of arsenic in the copper. However, with very high current density or other conditions producing an open or coarse-grained nodular deposit, mechanical entrainment of arsenic in the form of electrolyte, as well as in the form of slime, may be considerable. The experiments were run under the following conditions with various amounts of arsenic: copper in electrolyte, 42 g/liter; free acid in electrolyte, 160 g/liter; current density, 18 amp per sq ft; temperature of electrolyte, 55°C; time of electrolysis, 3 days.

Results of the Test

	No. 1	No. 2	No. 3
Arsenic in the electrolyte, g.p.l.	37.9	60.8	138.7
Arsenic in the cathode, per cent	0.0015	0.0022	0.0046

In the case of antimony, its maximum solubility in the electrolyte satisfactorily controls the situation.

When bismuth is abnormally high, it has been found necessary to reduce the acid content of the electrolyte to prevent contamination of the cathodes by salting out. Skowronski[8] reports that bismuth arsenate is formed when sufficient arsenic is present, but that while this, or any of the bismuth oxy-salts, have limited solubility, they are capable of supersaturating the electrolyte with bismuth to a high degree, especially when the acid content is high. The bismuth may be salted out on the cathodes from the supersaturated solution through small changes in temperature, circulation, or factors unknown. The precipitation on the cathodes is difficult to detect since it is invisible and has no effect on the conductivity. He states that one refinery had to reduce the acid content of the electrolyte to 130 grams per liter in order to satisfactorily reduce the bismuth content. Skowronski[8] refers to a refinery which treated anodes containing 0.015 to 0.03 per cent bismuth. At 200 grams per liter H_2SO_4 in the electrolyte, the cathodes contained as high as 0.01 per cent bismuth. At 130 grams per liter H_2SO_4 the bismuth content in the cathodes was reduced to 0.0002 per cent Bi. The Nkana refinery in Northern Rhodesia now reports a content of 1.68 grams of bismuth per liter in the electrolyte and an acid content of 125 grams of H_2SO_4 per liter.

In all probability, the major portion, if not all, of the arsenic, antimony, and bismuth found in cathodes is due to slime inclusions. These metals precipitate as slime in combination with each other, and the precipitates are the slowest settling ingredients of the slime. Antimony in particular is one of the chief components of float slime, which is a frequent source of trouble not only in contaminating copper, but also in forming hard incrustrations in electrolyte pipelines.

All three of the metals are dissolved from the anode electrochemically, but due to hydrolysis do not appear in the electrolyte as normal sulfates. Arsenic is present in the solution chiefly as arsenic acid or AsO_4^{---} ion, antimony as antimonious acid or SbO_3^{---} ion, and bismuth probably as a slightly soluble basic sulfate or bismuth arsenate, $BiAsO_4$. These salts, as previously mentioned, may be retained in the electrolyte in a supersaturated state. The theory that antimony is precipitated as a basic oxychloride is now generally discredited. Yu-lin Yao[9] presents an interesting proof of this point. The generally accepted theory is that all three of these metals are chiefly precipitated as arsenates. However, the ratio of antimony to arsenic in the slime is generally considerably greater than 1.675 to 1, the ratio of antimony to arsenic in $SbAsO_4$.

Bardwell and Lapee[10] discuss the effect of antimony in limiting the content of arsenic in solution. They show that the arsenic and antimony content of a solution can be simultaneously reduced by the addition of antimony trioxide. The tests were instigated by the fact that the arsenic content of the electrolyte invariably went up when the ratio of antimony to arsenic in the anode decreased.

Arsenides and antimonides have been isolated as ingredients in the anodes and anode slime. Being insoluble, they would be precipitated directly from the anode.

Behavior of Electronegative Metals

The other impurities in anode copper—lead, tin, nickel, cobalt, iron, and zinc—are all above hydrogen in the electromotive series and readily enter the solution by electrochemical reactions. All except lead may be chemically dissolved by the electrolyte to some extent. Lead and tin are precipitated in the slime as $PbSO_4$ and $Sn(OH)_2SO_4$.

Nickel is the predominating impurity in over half of the larger copper refineries. It readily accumulates in the electrolyte. Some nickel is found in the slime, since NiO is insoluble in dilute H_2SO_4.

Nickel is also found in the cathodes. The amount, relative to other impurities in the cathode, is greater than would be expected from the Ni content of the slime. This fact, plus the impossibility of electrodeposition of nickel, suggests the possibility of some electrolyte being occluded in or on the deposit. Figure 8-2 shows the relationship of nickel in cathodes to nickel in electrolyte at one refinery where the series system is employed. In comparing data from various refineries where the multiple system is employed, very erratic results were encountered. As a general average, the ratio of nickel in cathodes to nickel in electrolyte was about half of the amount shown for the series system. It should be noted that at the Copper Cliff refinery of the International Nickel Co., with 19.7 grams of nickel per liter in the electrolyte, the corresponding wirebar has a nickel content of only 0.0005 per cent. In all probability, the nickel content of the cathode is far more dependent on the physical nature of the cathode deposit than on the nickel content of the electrolyte.

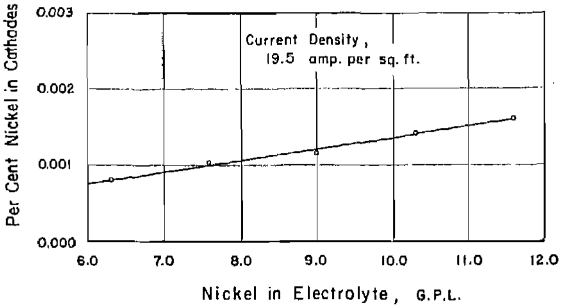

FIGURE 8-2. Relation of the nickel content of the cathode to the nickel content of the electrolyte, series system.

Cobalt, zinc, and iron also form highly soluble sulfates. Cobalt and zinc are not present in anode copper in amounts requiring special consideration. The iron content of anodes is also relatively low. For the most part, iron is present as ferric sulfate, $Fe_2(SO_4)_3$. This is a controversial point.

Theoretically, metals other than copper with soluble sulfates may accumulate in the electrolyte until their content exceeds that of copper before there is any danger of their codeposition with copper at the cathode. However, there is a limit to the solubility of SO_4^{--} ion in the solution and the accumulation of other sulfates in the electrolyte may cause curtailment of the copper and H_2SO_4 content to less than desirable amounts. Also the metal sulfates increase the resistivity of the electrolyte. All of the soluble electronegative metals tie up free H_2SO_4 when they enter the electrolyte and hence are factors in acid consumption. Whether metal sulfates other than copper are precipitated as slime or withdrawn to prevent impurity accumulations, the SO_4^{--} ion must be replaced by new H_2SO_4 since it is not liberated in any of the purification processes.

Passive Anodes

Although passive anodes are usually encountered when processing impure copper bullions, they can be caused by a lack of slime-forming constituents in the anode.

An example is the Noranda anode. In this case, Noranda anodes produce about 13 pounds of slime per ton of anodes corroded. This slime is fluffy in character. At electrolyte temperatures up to 61.5°C the slime adheres to the anode and serves as a barrier to the anode dissolving. This passivity can be overcome by increasing the temperature of the electrolyte to 66.5°C at the cell inlet. In spite of this high electrolyte temperature, some passivity of anodes is noted at the cold end of the cells. Covering the cells with plastic films of polyvinyl acetate serves to maintain electrolyte temperatures.

Cerro de Pasco has overcome passivity of anodes by the electrolysis of blister copper of high oxygen content (about 0.5 per cent). However, Noranda anodes of high oxygen content (0.3 per cent) were still passive. It is interesting to note that even though the oxygen content of the Noranda anodes was increased from 0.15 to 0.3 per cent, the copper content of the slime increased only about 10 per cent (from 5.5 to 6.0 pounds of copper per ton of anodes). This was explained by the fact that the slime adhered to the anode and enabled the metallic copper in the slime to be electrolytically deposited on the cathode.

Sufficient electrolyte circulation can also overcome passive anodes, but is not directly applicable in that it causes contamination of the cathode deposit with slime. Fortunately passivity is not frequently encountered in normal copper anodes.

Disposition of Anode Impurities

Table 8-3 shows the content of anodes being treated in the major refineries at the present time, the percentage of anode scrap, and the pounds of slime produced per ton of anodes electrolyzed. Table 11-2, p. 268, shows the content of anode slime from the various refineries. Based on these tables and the content of the cathodes, the following tabulation of disposition of the anode impurities is presented. This applies to major refineries only and not to abnormal operating conditions.

TABLE 8-1. PERCENTAGE OF METALS CORRODED FROM ANODES

	Into Slime			Into Solution			Into Cathodes		
Metal	Max.	Min.	Avg.	Max.	Min.	Avg.	Max.	Min.	Avg.
Ag	99.6	89.6	97.7	0.0	0.0	0.0	5.0	0.4	2.3
Au	99.8	94.5	98.6	0.0	0.0	0.0	3.5	0.2	1.4
Se and Te	99.0	96.0	97.6	0.0	0.0	0.0	4.0	1.0	2.4
Pb	99.4	97.5	98.3	0.0	0.0	0.0	0.5	0.6	1.7
Ni	10.2	0.4	3.7	98.7	88.6	94.9	3.0	0.5	1.4
As	46.7	8.5	24.7	90.2	52.6	73.8	2.3	0.7	1.5
Sb	90.0	32.8	57.6	68.4	7.3	40.4	3.6	1.2	2.0

The percentage of anodic impurity entering the cathode deposit tends to increase as the impurity content of the anode decreases. The wide range of variation in the proportions of antimony and arsenic entering the slime is readily understandable. As previously mentioned, the precipitation of arsenic depends to some extent on the antimony content of the anode. Since the amount of antimony entering solution is limited by its solubility, the smaller the amount of antimony in the anode, the greater the percentage thereof will enter the electrolyte. Also, a heavy withdrawal for purification, which tends to keep the content of the electrolyte low, will favor increases in the proportion of antimony entering solution.

The following tabulation indicates the range of impurities in cathodes at the major refineries:

TABLE 8-2. RANGE OF CATHODE IMPURITIES

Silver	0.05	to	0.90	oz/ton
Gold	0.004	to	0.024	oz/ton
Selenium	0.0002	to	0.0015	per cent
Tellurium	0.0004	to	0.0008	per cent
Lead	0.0005	to	0.0013	per cent
Nickel	Trace	to	0.0015	per cent
Arsenic	0.0004	to	0.0011	per cent
Antimony	0.0005	to	0.0014	per cent
Bismuth	Trace	to	0.0002	per cent

Operating Conditions

In the data of the various refineries shown in Table 8-3, the following ranges in operating data are indicated:

	Maximum	Minimum
Current density, amp per sq ft	25.5	11.2
Temperature of electrolyte, °C	65	48
Copper in electrolyte, g/liter	52.0	34.5
Free acid in electrolyte, g/liter	225.0	125.0
Nickel in electrolyte, g/liter	21.1	1.5
Iron in electrolyte, g/liter	6.0	0.2
Arsenic in electrolyte, g/liter	12.0	0.5
Antimony in electrolyte, g/liter	0.8	0.3
Chlorine in electrolyte, g/liter	0.045	0.003
Specific gravity of electrolyte	1.28	1.18
Rate of circulation, gal. per min	6.0	1.7
Pounds of glue added per ton of cathodes produced	.07	relatively nil

The range gives some idea of the variations that it is possible to employ in meeting variations in anode contents and cost factors. In any case, the optimum depends on the imposed conditions. In general, the following facts obtain within the limits shown above:

For any given production, the power consumption increases but the size of the required installation and time required for refining decreases with increase of current density.

Increase of temperature of the electrolyte decreases the power consumption but increases the heat requirement. It also increases the solubility of the anode in the electrolyte and makes possible an increase in copper and acid content.

Increase of free acid in the electrolyte decreases the power consumption, but if carried to excess will curtail the copper content of the electrolyte, since the total SO_4 content is limited.

Increase in copper in the electrolyte increases the power consumption, but tends to improve the structure and purity of the copper deposit.

The behavior of the various impurities has been discussed. The cell voltage, and hence the power consumption, increases with the impurity content of the electrolyte, as does the danger of contamination of the cathode.

Circulation of the electrolyte is essential. The rate of circulation must be sufficient to maintain the desired temperature and to prevent stratification of the solution in the cells, undue depletion of copper ions near the surface of the cathodes, and too high concentration of copper ions near the surface of the anodes. The electrolyte is heated in the head tanks, sumps, or heat exchangers and loses temperature as it circulates through the feed lines, cells, and return launders. However, the higher the rate of circulation, the greater the tendency to retard the settling of the slime, and hence the greater the possibility of cathode contamination.

In the majority of refineries, the electrolyte enters at the bottom of the tanks and is withdrawn at the top. Thus, the direction of electrolyte circulation opposes the settling of the slime. In several major refineries, top-to-bottom circulation is employed. They report a general improvement in regard to cathode contamination and trouble from float slime when employing this type of circulation. They do not experience any extra difficulty in avoiding stratification or in maintaining the proper solution level when starting circulation in cells that have just been filled.

Glue and other addition agents improve the density and smoothness of the copper deposits. The effect of chlorine is to improve the structure of the cathode deposit and precipitate silver from the electrolyte.

Addition Agents

All electrolytic copper refining cells employ a sulfuric acid-copper sulfate electrolyte. When nothing is added to the electrolyte, the cathode deposit is soft and coarsely crystalline[12]. This type of deposit entraps impurities and is prone to develop nodular formations, which, as discussed later under the subject of current efficiency, are a frequent cause of short circuits. Therefore, to obtain smooth, firm cathode deposits, all refineries use one or more addition agents. Although each refinery must develop its own combination of addition agents which best suits its purposes, glue is used by all. It refines the grain size of the cathode deposits by providing nuclei for crystal formation. In the multiple system, glue is used in amounts as small as 0.012 pound (at Norddeutsche Affinerie) to 0.70 pound per ton of copper deposited (at Cerro de Pasco). The cathode polarization caused by glue is dependent on the amount used and usually in practice amounts to about 30 to 45 millivolts, or about 10 to 20 per cent of the normal cell voltage. In spite of the increased cell voltage and the consequent increased cost of power, the advantages of the improved cathode deposit demand the use of glue.

The glue is dispersed in water and usually trickled into the electrolyte continuously throughout the entire day at the rate of about 4 parts glue per million parts of electrolyte per day. The glue definitely enters the cathode deposit by being absorbed between the grains and forming a high-resistance film. This tends to round any nodules formed.

Much work has been done on the development of addition agents to supplement or replace glue. As yet, experimentally, it has not been possible to replace glue completely with anything which gives a comparable cathode deposit, without increased cathode polarization and thus increased power cost.

Glue is a protein, consisting of a mixture of many amino acids. Some of these are effective addition agents. Hydrolysis of glue with either acids or bases prior to addition to the copper refining electrolyte partially removes the excessive cathode polarization encountered when using untreated glue. Unfortunately the cathode deposits with hydrolyzed glue are not as good as those with regular glue.

It appears at the present time that a good addition agent is one which causes cathode polarization. Although glue is the best addition agent, it is not used alone. The most commonly used supplemental addition agent is a variety of sulfite lignone liquor, known under such trade names as "goulac," "bindarene," and "lignone." It is commercially produced as a solid or as a concentrated solution. Its use as an addition agent was patented by Colcord.* Goulac, or its equivalent, is used in amounts of about 0.2 to 0.6 pound per ton of cathode copper deposited.

Goulac acts as a buffer. It does not refine grain size nor does it have much effect on cathode polarization. Should excessive glue be added to the electrolyte, goulac aids in counteracting this excess, so that cathode current efficiencies and hardness are not adversely affected. The disadvantage of goulac is that it tends to form insoluble compounds in the electrolyte which cause plugging of solution lines.

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* U. S. Patent 1,544,726.

Other supplemental addition agents are used. Casein, like glue, is a protein. It is being used by the Raritan Copper Works at Perth Amboy and its use has been patented by Skowronski and Mosher.* Since casein is not readily soluble in the electrolyte, it is partially hydrolyzed with acid before addition. Raritan uses both glue and goulac with casein. At E. R. & S. in Australia, equal amounts (0.06 pound per ton) of glue and casein, the latter hydrolyzed with soda ash, are used as addition agents, while at Mt. Lyell in Tasmania casein with glue and sulfonated castor oil are used.

Thiourea is finding good acceptance at Outokumpu and Bolidens and is reported to diminish cathode nodulation, but to increase the striated appearance of the cathode.

The use of "Avitone," a sulfonated petroleum product and a surface active agent, as an addition agent was developed at Canadian Copper Refiners Ltd., and has been patented as U. S. Patent 2,660,555. Avitone increases cathode polarization only slightly and does not form insoluble compounds with electrolytes. When C.C.R. started using Avitone, it was possible to reduce the amount of glue from 0.12 to 0.09 pound per ton of cathodes deposited.

Complete data on the addition agents now being used by all major copper refineries are given in Table 8-3.

Salt can be considered an addition agent. Up to approximately 30 mg per liter, the critical value depending on other conditions, the action of chlorine is beneficial. Above the critical value it causes needle-like formations in the deposit. These can form and grow with surprising rapidity in many cases, causing short circuits before they are detected. Yu-lin Yao[13] states that the grain size of the copper deposit decreases up to a concentration of 15 mg of chlorine per liter and then increases above that point. He also shows that the cathode polarization increases up to the same critical concentration and above that decreases. Precipitation of chlorine as AgCl and Cu_2Cl_2 may aid in taking care of some of the excess of chlorine above the critical concentrations.

Two common methods are used to evaluate addition agents. The first measures the amount of carbon dioxide evolved by digesting electrolyte with dichromate to oxidize all carbonaceous matter. A typical analysis is about 0.9 to 1.2 grams of CO_2 per liter of electrolyte. In the second method, permanganate is used to determine the organic reducing power of the electrolyte.

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* U. S. Patent 2,556,635.

However, the most satisfactory method to test addition agents is to observe carefully the day-by-day appearance of the cathodes. No general rule can be laid down for all copper refineries as to what addition agent they should employ. In this regard, it is most essential that at least one commercial section with an entirely separate electrolyte circulation be provided so that addition agents can be properly evaluated without jeopardizing the operation of the entire tank room.

In general, it is good practice when in doubt about addition agents to reduce rather than increase the quantity being added, since too much is always worse than too little.

Electrolytic Tank-Room Layout and Operating Procedure, Multiple System[14]

In the multiple system each individual tank is a cell unit, all anodes and all cathodes in the tank being connected in parallel. The anodes and cathodes are placed alternately in the tank. Using conventional terminology for the direction of flow, the total current delivered to each tank is distributed to the anodes through a common bus or distributor bar supported on one of the side walls of the tank, and is delivered by the cathodes to a common bar on the opposite side wall. The anodes are cast with supporting lugs, and one lug of each anode rests on the positive bar. The other lug of the anode rests on a cap board of wood or other insulating material, which is supported on the negative side wall. The cathodes are suspended by copper loops from copper bars. These suspension bars span the tank, one end resting on the negative bus or distributor bar and the other on a cap board on the positive side wall (see Figures 8-3 and 8-4).

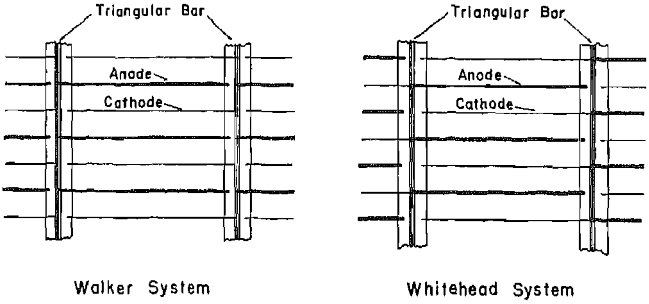


FIGURE 8-3. Tank connections.

With the exception of the Great Falls refinery, the tanks are arranged in tiers, and adjacent tanks in a tier have a common side wall. The tiers are arranged in sections, two tiers to a section (see Figure 8-5). All the tanks in each tier are in series electrically and the two tiers are in series. The distributor bar on the common wall of adjacent tanks acts as the negative bar of one tank and the positive bar of the next. With the tier construction, there are two types of electrode arrangement (see Figures 8-3 and 8-4). In the Walker arrangement, there is no direct connection between the cathodes in one tank and the anodes in the next. The distributor bar carries all the current that passes from the cathodes in one tank to the anodes in the next. No part of the bar carries the full current, but only that part passing between adjacent electrodes. Hence the cross section of the bar is relatively small. For the purpose of providing better contacts, the bar is triangular in cross section. In the Whitehead system, the cathodes in one tank make direct contact with the anodes in the next, one end of each cathode suspension bar resting on an anode lug or in a groove cast in the lug. The groove, known as the Aubel or Baltimore groove, is now in almost universal use where the Whitehead

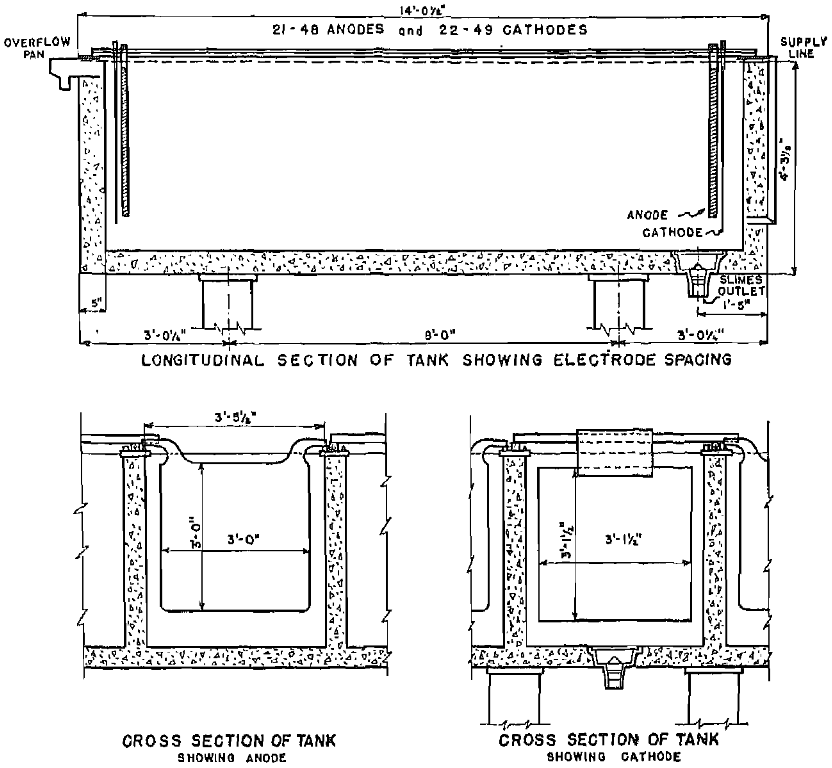


FIGURE 8-4. Typical multiple tank, Whitehead single contact, Baltimore groove.

system is employed. In this system, the anode lugs rest on a distributor bar which serves to adjust any mal-distribution of current between parallel electrodes. At the Great Falls refinery, the tanks are arranged in series, end to end with two bus bars to each tank. The positive bar of one tank is an extension of the negative bar of the preceding tank.

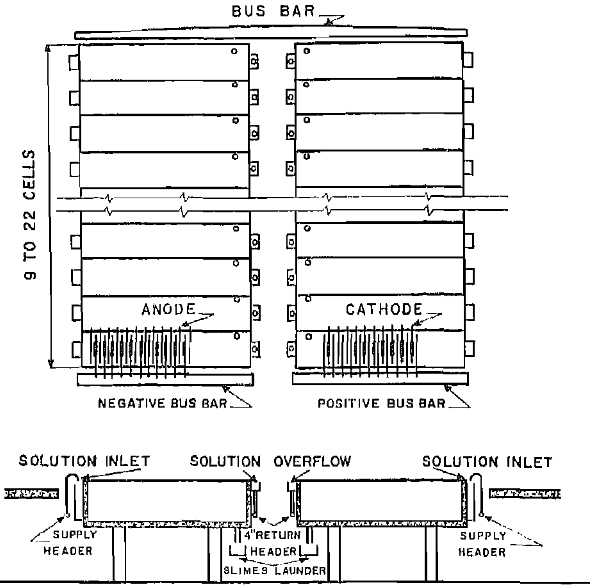


FIGURE 8-5. Typical multiple-tank section, two-tier arrangement.

Table 8-3 presents data in regard to the major electrolytic refineries. The data include system of electrode arrangement; size, weight, and life of anodes and cathodes; current density and cell voltage; current and power efficiency; tank size and construction; and general operating conditions.

Multiple anodes vary in weight from 350 to 850 pounds, with variations in effective surface area (each side) of from 26 by 35 inches to 35¾ by 39½ inches, and in thickness of from 1¼ to 2¾ inches. In most recently constructed tank rooms, there appears to be a tendency to adopt a standard anode, 36 by 36 inches in surface area, and 625 to 700 pounds in weight (1¼ to 1¾ inches thick). Anodes are not completely consumed before replacement, due to inevitable inequalities in corrosion and in thickness as cast. Attempts to decrease the anode remnants too greatly result in too much anode scrap in the slime, damage to tank linings by the fall of heavy pieces of anode, and irregularities in current distribution throughout the cell with the attendant decrease of power efficiency. The anode scrap, including the weight of the lugs, is from 13 to 25 per cent of the original weight of the anode. The life of the anodes varies with the weight and current density. The average life with normal operations is approximately 28 days, which conforms to an economical production cycle and the general arrangement of section units in the major refineries. The spacing of adjacent anodes is from 3½ to 7 inches, center to center, usually 4 to 4½ inches, with a distance between anode-to-cathode faces of from 1.05 to 1.50 inches on the first crop of cathodes and 1.34 to 1.80 inches on the second, if the production is completed in two runs. To reduce power cost, some refineries close the anode spacing after the first crop of cathodes has been drawn.

Anodes are loaded by section or half section (tier) lots, generally the latter, and two crops of cathodes are produced during the life of the anodes. With high-grade (high precious-metal content) anodes, smaller sections are frequently employed and more than two crops of cathodes produced per loading of anodes. The number of anodes per tank varies from 21 to 48 (usually 30 to 38) and the number of tanks per tier from 9 to 22 (usually 16 to 18). Except in the production of starting sheets, the electrode at each end of the tank is a cathode, and hence there is one more cathode than anode per tank. The average weight of the full-growth cathode (two-crop basis) is approximately 43 per cent of the weight of the anode. This includes the weight of the starting sheet.

For every crop of cathodes a set of starting sheets must be provided for receiving the initial deposit of copper. These sheets are electrolytically produced by a 24-hour deposition of copper on the surface of a rolled copper blank. The blanks are placed as cathodes between soluble anodes in the stripper tanks. Anodes of normal composition but slightly larger in surface area than those in the commercial tanks are used. Stripper tanks are of the same size and electrode arrangement as the commercial tanks and generally the arrangement in tiers is the same. The electrolyte is generally slightly higher in copper and lower in impurities, and carries more addition agent than the commercial electrolyte. A firm deposit is requisite. The surface of the blank is covered with a light film of oil before being subjected to electrolysis. This prevents firm adherence of the deposit to the surface of the blank. A new blank must be coated with amalgam or lampblack when first used, otherwise the oil film will be ineffective. The blanks are from ⅛ to $^3/_{16}$ inch thick and riveted to a suspension bar. A groove ¼ inch from the side and bottom edges facilitates the separation of the sheet on the surface of the blank from the deposit around the edges and results in the production of a sheet with straight, even edges. The sheets are approximately 1 inch larger and wider than the commercial anode. This helps to counteract the excess density due to stray current that concentrates on the cathode periphery. The sheets are suspended from loops which are cut from starting sheets. The loops are clipped to the top of the sheets by special clip machines. Two types of suspension loops are used, the single large loop in the center of the sheet, or two narrow loops at the quarter points.

The general arrangement of the major tank rooms is similar in most respects. The electrolytic tank sections are located in one or more parallel crane bays on either side of a central bay which houses the solution sumps, pumps, and head tanks. (Figures 8-6 and 8-7). In the majority of installations, the tiers of tanks run parallel to the crane runways as shown in the illustration. In others, they run at right angles thereto.

The tanks are usually built of reinforced concrete, cast in place or cast in sections and assembled. Some all-wood tanks are still in use, and some tanks have concrete side walls with wood bottoms. For size of tanks see the tabulation. The tanks are lead-lined generally with 8-pound 6 per cent antimonial lead, and are provided with weep holes through the concrete for detection of leaks, and with drain outlets for the removal of slime. Figure 8-4 shows the construction of a typical tank, Whitehead arrangement. In modern construction, the cells are supported by concrete columns with bases in the basement floor. In order to insulate the tanks from the ground and surrounding floors, the columns are capped with heavy plates of glass or vitreous tile, cushioned with rubber or fiber pads, and covered with lead shields. The tanks are independent of the working floor, which is 18 to 42 inches below the tops of the tanks. The top of the tank walls is covered with mastic, and on this rest the cap boards. The base of the tanks should be of sufficient height to provide enough slope for the slime and solution launders, between any of the tank outlets and the sumps in the central bay. The basement floor is usually mastic-covered, and drains to pits in the central bay.

The tank sections are connected in series in electrical circuits, with sufficient tanks in each circuit to give a total voltage of from 50 to 300. The load on the circuit varies from 5,000 to 20,000 amperes. Power is supplied by motor-generator sets or rotary converters, usually several sets in parallel. Because of the flexibility required in meeting load variations and to avoid high power conversion losses, especially designed equipment is frequently used.

The solution is circulated through each tank at rates varying from 1.7 to 6.0 gallons per minute. There are generally from 100 to 500 tanks in a solution circuit, and the flow through all the tanks in the circuit is in parallel. At Great Falls the solution flows through cascades of 5 tanks each, with 24 cascades in parallel in a solution circuit. The general direc-

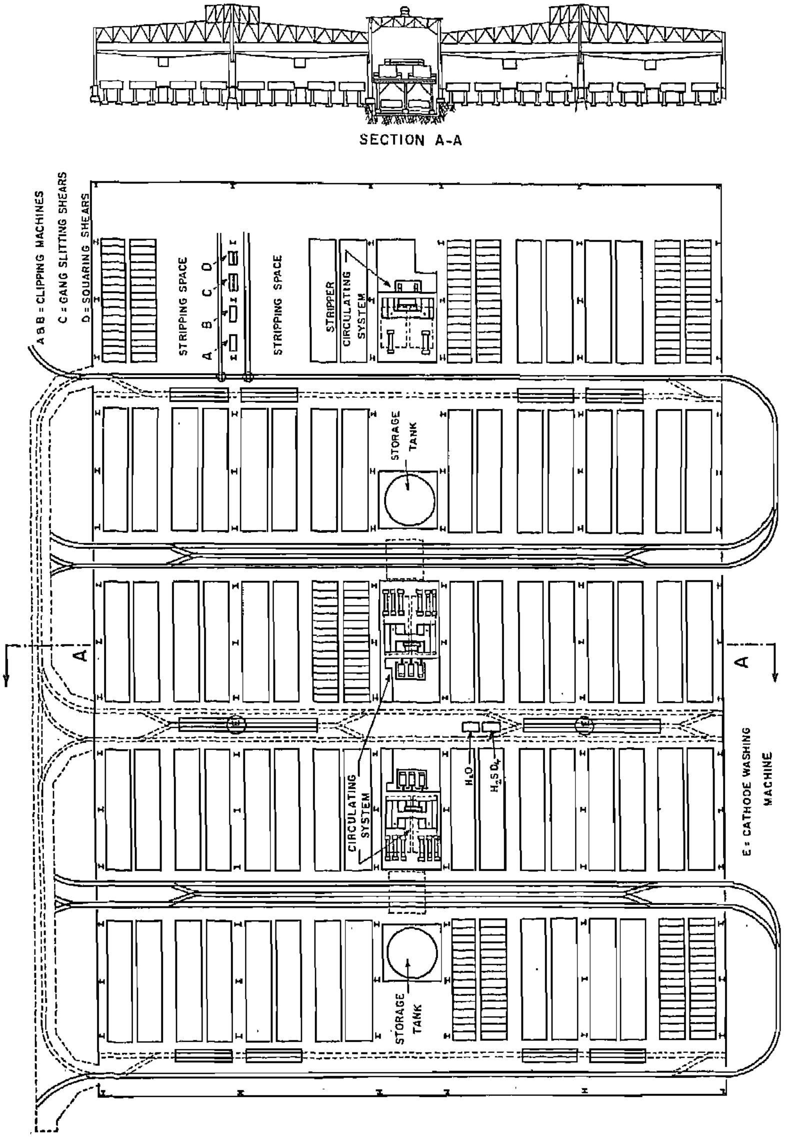


FIGURE 8-6. Layout of electrolytic tank room.

tion of flow through the individual tanks is perpendicular to the electrodes, solution entering at one end and leaving at the other. Solution from the tanks is returned by gravity through a system of pipes, or covered launders and pipes, to sumps, from which it is pumped to head tanks and thence by gravity through a system of pipes to section headers which feed the individual tanks in the section. The feed to the individual tanks and the flow from these tanks is through rubber hoses. The hose ends are not allowed to touch the solution in the tank or in the return launder or pipe. At these two points in the circuit, the solution falls freely through the air, to reduce stray-current losses. Although the major portion of the solution lines or launders is lead or lead-lined, sections of porcelain, glass, rubber, or plastic pipes or pipe connections are frequently used for the same reason. The sumps and head tanks are of wood or concrete and lined with antimonial lead. The pumps are generally of the horizontal centrifugal type and of special acid-resistant materials. The solution is steam-heated by coils located in the sumps or head tanks, or by special tubular heat exchangers in the circulation system between the two tanks. Karbate tube heaters are being adopted in the newer installations. The average temperature of the electrolyte is about 60°C at the inlet and about 55°C at the outlet of the cells.

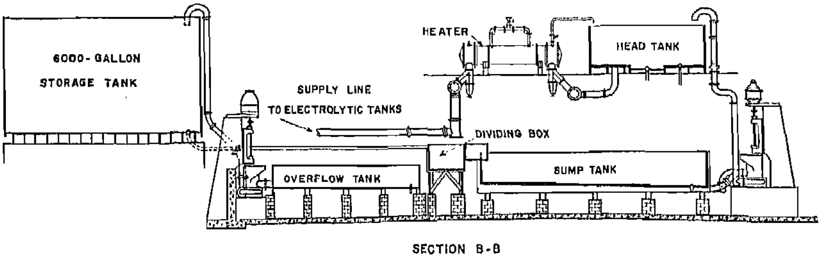


Figure 8-7. *Arrangement of head tank, storage tank, and pumping system.*

The tanks are serviced by overhead traveling cranes, carrying multi-hook racks (Figure 8-6). The arrangement is such that an entire tank load of anodes or cathodes can be loaded or removed at one lifting. Anodes are transported in rack cars holding one tank load of anodes correctly spaced for placing in the tank. Cathodes and anode scrap are transported on flat cars. Cathodes are washed by submersion in steam condensate or sprayed by high-pressure hot water, or both. Special cathode washing machines are generally employed. The anode scrap is washed with high-pressure sprays.

The slime is sluiced from the cells through a series of lead-lined launders to the slime pit or pits, where it is screened and collected for treatment.

The anode loading is usually scheduled so that when the anodes in one tier of a section are ready for changing, those in the other tier are half consumed. Contemplating two-crop production of cathodes, the following procedure is typical. The power is cut off the section by a shunt across the two bus bars. The cathodes are then removed from the tanks in both tiers. The solution is siphoned or drained from one tier, the anode scrap removed, and the slimes sluiced from the tanks. This tier is then reloaded with new anodes and filled with electrolyte. Both tiers are then loaded with starting sheets and placed under current.

Starting sheets are produced daily from all tanks in the stripper sections. The production is handled without interruption of current by removing, stripping, re-oiling, and replacing half of the blanks in a tank at one time. The section is cut out only for changing anodes and removal of slime.

Electrolytic Tank-Room Layout and Operating Procedure, Nichols Series System[15]

Since the installation at the Laurel Hill plant of the Phelps Dodge Refining Corporation is now the sole surviving series system in operation, description will be confined to the Nichols arrangement and the operating procedure at that plant. Figure 8-8 and the data in Table 8-3 present the pertinent details.

In the series system, each individual tank contains a series of cells, all electrodes except the first and last in the tank being bipolar. With reference to Figure 8-8, all the current enters the solution through the bar and set of electrodes suspended therefrom at the left or positive end of the tank and leaves the solution through the bar and corresponding set of electrodes at the right or negative end of the tank. The current passes through the solution and intermediate sets of electrodes depositing copper on the left or negative face of each electrode and dissolving copper from the right or positive face. The intermediate electrodes are suspended by copper links from iron bars, but these bars make no electrical contacts. The backs or negative faces of the bipolar electrodes (anodes originally) are sprayed with a film of 25 per cent sodium resinate solution before being placed in service. This prevents firm adherence of the deposited copper to the electrode surface.

Five electrodes are supported from each bar. The first bar is of copper and serves as the positive bus bar of the tank. The anodes are suspended therefrom by copper links and weigh approximately 150 pounds each. They are heavier than the intermediate anodes because they will be

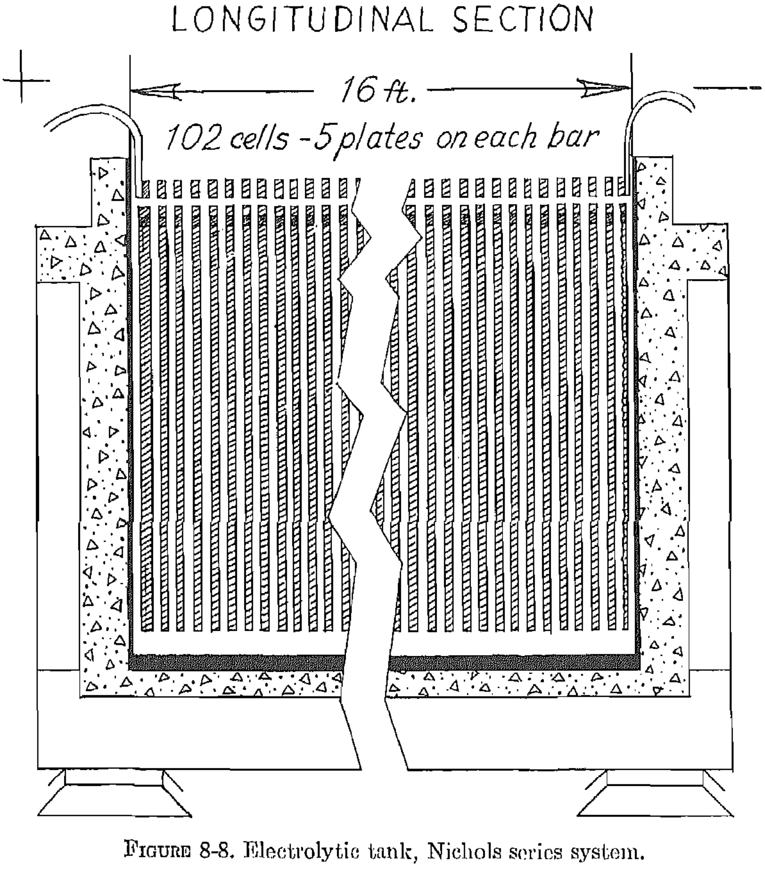


Figure 8-8. Electrolytic tank, Nichols series system.

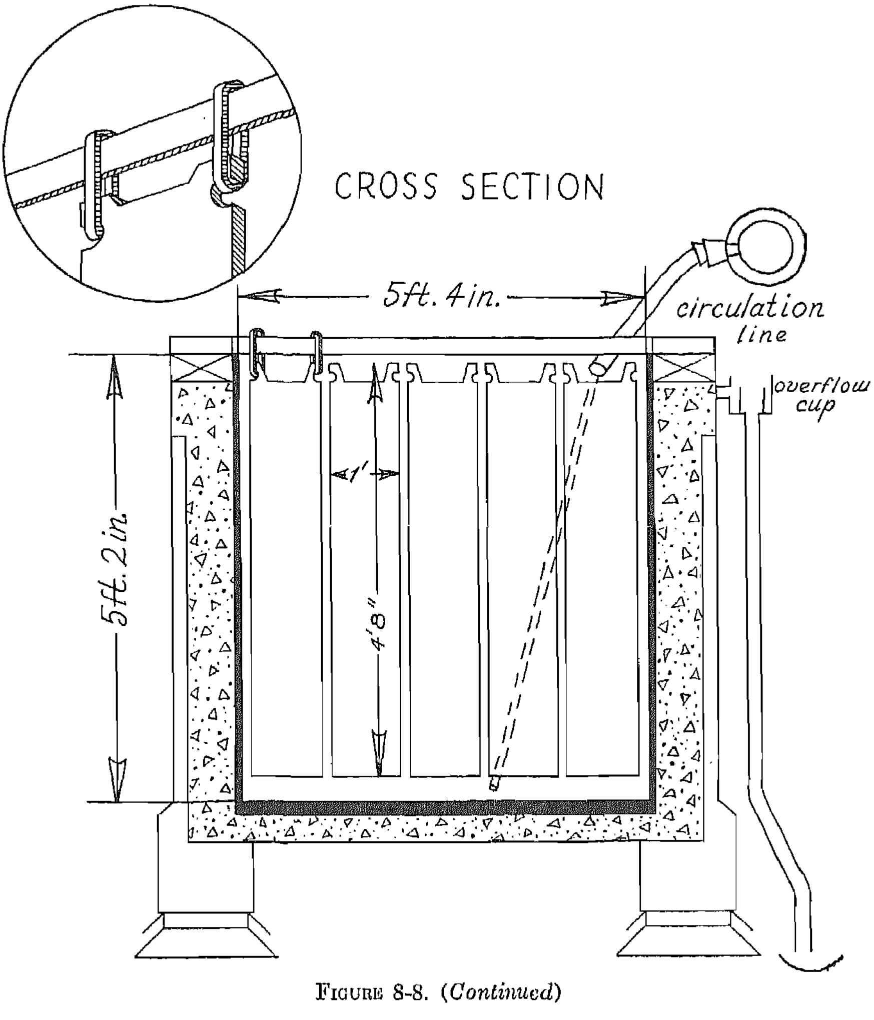


FIGURE 8-8. (*Continued*)

subjected to a relatively greater corrosion. The intermediate anodes weigh approximately 110 pounds. All anodes are hand-cast with ears and are remarkably uniform. This is of utmost importance in the series system. The lugs are formed by slots punched in these ears. The effective size of the anode is 56 by 12 by $\frac{9}{16}$ inch. The spacing center to center of adjacent electrode sets is $1\frac{13}{16}$ inches and the distance face to face between electrodes $1\frac{1}{4}$ inches. The last set of electrodes in the tank are starting cathodes. When first loaded to the tanks, these weigh approximately 45 pounds. They are produced by stripping light deposits from partially consumed anodes. Certain tanks are devoted to the production of these starting cathodes. Two crops of starting cathodes are produced from one loading of anodes. A complete tank loading consists of 5 heavy plates (anodes), 505 regular anodes, and 5 starting cathodes, and so loaded constitutes 102 cell units.

In the normal procedure, one loading of anodes produces one crop of cathodes, the duration of the run depending on the current density. The complete cycle is generally 21 to 28 days. Electrolysis is continued until the anode is from 85 to 90 per cent consumed. The tank is then cut out, solution siphoned off, and the plates washed in the tanks by high-pressure sprays that can be inserted and moved up and down between the electrodes. The plates are then unloaded and the backs (anode remnants) stripped by hand from the deposit. The cathodes will normally weigh from 92 to 102 pounds each. The slime is drawn from the tanks, transported to the mud house, screened, and the copper removed by a simple aeration leach with electrolyte. The leach solution is returned to the circuit or sent to the copper sulfate plant.

In the near future, the tanks will be entirely of assembled precast reinforced concrete. These are lined with asphalt, mastic, and blown oil, since a metallic lining would tend to act as a bipolar electrode. On account of the nature of the lining, the temperature of the electrolyte is limited to approximately 50°C (130°F). Compared with temperatures employed in the multiple system, this would appear as a handicap in the matter of electrolyte resistivity. However, the contact resistance is practically nil in comparison with the contact resistance of the multiple system. The tanks are mounted on lead-capped tile piers. The tank side walls are capped with stationary wooden spacing blocks. These form slots into which the ends of the suspension bars are fitted. Spacing blocks are also inserted between adjacent bars at the center of the tank.

The electrolyte flows by gravity from receiving tanks through lead-lined heat exchangers to 12-inch manifolds and thence through 4-inch lead main feed lines to the individual tanks. The solution is introduced to the tanks through glass tubes which carry the solution to within 5 to 8 inches from the bottom of the tank. The rate of flow through the tank averages 3.5 gallons per minute. The solution from the tanks flows by gravity through lead-lined gutters cut in the floors, to wood, lead-lined settling pits, from which it is pumped back to the receivers.

Normally, from 18 to 22 tanks are electrically connected in series and two parallel series of an equal number of tanks constitute a circuit. Direct current is supplied by rotary converters. The tanks are served by overhead cranes, capable of handling a tank of electrodes in six rack loadings.

The impurities in the electrolyte are controlled by withdrawal of solution for the production of copper sulfate. The impurity and copper content of the electrolyte is maintained at lower levels than is customary with the multiple system. The free acid content is slightly higher. The use of glue and chlorine is negligible in comparison with the practice in multiple tank rooms. High cathode polarization, which would be the result of glue additions, tends to promote the growth of a sheet of copper along the bottom of the electrodes. The current efficiency averages approximately 22 per cent less than in the multiple system, but the cell voltage is approximately 67 per cent of that in the multiple system operating under similar conditions.

Current Efficiency

At 100 per cent current efficiency, 382.5 ampere-hours of electricity will dissolve 1 pound of copper from the anode or deposit 1 pound of copper on the cathode, based on the behavior of copper as a bivalent metal. This is equivalent to 0.6274 pound of copper per ampere-day. In industrial work, the unit of electricity for current efficiency calculations is the ampere-tank-day.

Where the multiple system is employed, the cathode production is weighed by sections or half-sections and not by tanks. The ampere-tank-days utilized in the production from a section is equal to (the number of tanks in the section) × (the average ampere load on the circuit) × (the days consumed in the production). In the series system, the ampere-tank-day is the average ampere load on the circuit multiplied by the number of cells in the tank.

Under operating conditions neither 100 per cent anode efficiency nor 100 per cent cathode efficiency is realized and the efficiencies at the two electrodes are seldom equal. Anode current efficiencies are seldom calculated or directly referred to. The term "current efficiency" is generally accepted as denoting cathode current efficiency.

The factors that reduce the cathode current efficiency are (1) short circuiting, (2) stray current losses, (3) chemical re-solution of the deposited copper, and (4) electrochemical reactions at the cathode that do not involve the deposition of copper.

Short circuiting is generally the predominating factor in the loss of current efficiency. Under normal conditions, losses directly attributable to causes other than short circuits do not amount to more than 2 to 4 per cent. When employing the multiple system, the average current efficiency realized in commercial operations is approximately 92 per cent. Contacts between anodes and cathodes in the same cell are caused by bent or warped starting sheets, poorly aligned electrodes, or nodular and needle formations that develop in the cathode deposit. The starting sheets are usually straightened before loading. Since there is a tendency for the sheets to warp until they have received 12 to 24 hours' deposition of copper, the practice in most refineries is to straighten shortly after loading and sometimes again after the sheets have been under current for 24 hours.

Any irregularities on the surface of the starting sheet are magnified during the deposition of the copper and tend to form nodular growths. Due to stray current, the current density at the edges of the cathode is slightly greater than the average over the surface. This results in a somewhat heavier than average deposit along the edges, which are the most frequent location of nodular growths. In some cases, nodular growths are attributed to adhering slime particles. Float slime will cause leaf-like growths to form near the solution line. These spread out rapidly and may cause short circuits within a few hours. High chlorine is one but not the only source of the needle-like formations that also develop rapidly. Irregularities develop during the growth of the deposit that cannot be traced to any definite source. Increasing the current density decreases the grain size of the deposit[16], all other conditions being equal. Irregularities develop more rapidly with faster deposition rates; hence, the tendency for short circuits increases. However, in the range of commercial operations, high current density, in itself, is not a direct factor in lowering current efficiency and there is no consistent relationship between current efficiency and current density.

The control of short circuits is a matter of efficient and regular inspection service. The extent to which inspection work is employed is determined by the relative costs of power and labor. Inspection for short circuits is carried out by special portable meters which detect abnormalities in current distribution between parallel electrodes, and by systematically passing sticks between the electrodes. Recently the Gauss meter has come into use for inspection work. This meter is somewhat similar to a galvanometer. When the meter is held above a cathode suspension bar, deflections of the indicator needle show any excess or shortage in the amount of current passing through the electrode. An excess denotes the possibility of a short circuit while a shortage indicates the probability of poor contacts.

In the modern copper refineries, stray current losses amount to from 2 to 3 per cent of the total current delivered to each circuit, even when all leads, tanks, pipelines, and launders are perfectly insulated. Leaking tanks, lines, and launders will aggravate the losses. Wet or sulfate-covered cell tops or cap boards will promote stray current losses. However, the chief source of stray current loss is in the current carried from the cells in the circulating electrolyte. In spite of many improvements that have been made in the insulation of tanks, and the introduction of nonconducting materials in the circulation system, the stray current losses account for an average of about 2.5 per cent loss in current efficiency. In some refineries, an allowance for stray current loss is deducted from the actual ampere load when calculating current efficiency.

The Central Research Laboratory of the American Smelting & Refining Co.[17] has carried out several hundred laboratory tests to determine the effect of various factors on current efficiency. Tests were conducted using both synthetic electrolytes and electrolytes taken from the solution system in the tank room. A number of tests were run to establish each point. The results and conclusions follow:

(1) At a current density of 18.6 amp per sq ft and electrolyte temperature of 35°C, the current efficiency obtained with commercial or synthetic electrolytes is 100 per cent within experimental limits of error and for the range of content employed in normal operating conditions.

(2) The same is true with a current density of 30 amp per sq ft. This indicates that current density has no direct effect on current efficiency.

(3) At a current density of 18.6 amp per sq ft, temperature of 60°C (140°F), and normal composition of electrolyte with the exception that iron was excluded, the current efficiency averaged 97.5 per cent.

(4) At a current density of 30.0 amp per sq ft, and other conditions the same as in (3), the current efficiency averaged 98.5 per cent.

By comparing the results of (3) and (4) it appears that the loss in current efficiency was in direct proportion to the time of deposition and the cathode area and independent of the current density. The results point to oxidation and re-solution of the cathode, which could only be attributed to oxygen dissolved in the electrolyte.

(5) Tests made without current flowing indicated a loss in the cathode weight equal to the apparent loss by re-solution during deposition in an equal interval of time. This corroborates the previous tests which indicated that the current efficiency loss by corrosion was a function of time and not current density.

(6) Tests were made at 18.6 current density and 60°C to determine the effect of ferric iron. The loss of current efficiency with ferric iron in the solution was in excess of the loss that could be attributed to oxygen alone, but it was impossible to correlate the loss directly to the quantity of Fe^{+++} ion that was reduced to Fe^{++} ion.

(7) Bubbling air through the solution increased the loss of current efficiency but apparently had no effect in oxidizing Fe^{++} ion to Fe^{+++} ion. In all probability, air entrapped in the electrolyte does not act directly to oxidize the copper electrodes, Cu^{+} ion, or Fe^{++} ion, but acts as a reservoir to replenish oxygen in solution when it is converted to H_2O by chemical reaction. This emphasizes the importance of eliminating air in the circulating electrolyte. The solubility of oxygen in the electrolyte is relatively low and in commercial operations the ratio of volume and surface area of the electrolyte to the surface area of the electrodes is much less than in the test cells. Hence, the relative loss in current efficiency due to the direct or indirect effect of oxygen should be less than in the test cells, providing air in the electrolyte can be avoided.

(8) Current efficiency was not affected by changes in H_2SO_4 concentration from 150 to 220 grams per liter, nor by changes in copper concentration from 15 to 45 grams per liter.

(9) Tests indicated that AsO_4^{---} ion might have had some beneficial effect in inhibiting oxidation by Fe^{+++} ion but had no direct effect on cathode current efficiency. The results were not of sufficient magnitude to be conclusive.

(10) The content of nickel within normal ranges of concentration had no effect on current efficiency.

The effect of ferric iron on current efficiency is an extremely controversial subject. Reports from several sources in regard to laboratory tests indicate that with soluble copper anodes, normal temperatures, and normal contents of electrolyte and current density, ferric iron up to 3 grams per liter has no effect in reducing current efficiency[18]. The erratic behavior of iron in H_2SO_4-$CuSO_4$ electrolyte may explain the apparently contradictory results.

It is understood that the effect of iron on current efficiency in a cell with insoluble anodes cannot be compared with the effect in a cell with soluble anodes. However, there may be some analogy between the tendency for erratic behavior of iron in the electrowinning process and the apparent inconsistencies noted in regard to the effect of iron in the refining process. During the passage through the cell or series of cells, Fe^{+++} ion may be reduced to Fe^{++} ion by reaction with Cu and be re-oxidized to Fe^{+++} ion by oxidizing agents present. This cyclic reaction may be repeated several times before the iron leaves the cell or last cell in the cascade. Each reduction of Fe^{+++} ion corresponds to the re-solution of an equivalent amount of copper. At other times in the same system and with no apparent change in conditions, the iron appears to be stabilized in the form of Fe^{+++} ion or Fe^{++} ion or both and does not cause re-solution of the copper. Some changes in conditions that have gone undetected, *i.e.*, an increase in the amount of some catalytic agent, or decrease in the amount of some inhibiting agent, may have upset the balance between oxidizing and reducing agencies and resulted in the activation of the iron. As an illustration, at Chuquicamata[19], the presence of small amounts of molybdenum in solution was found to be one cause of increased iron activity, invariably connected with periods of low current efficiency.

Lowering the copper content by depositing out copper may entail deposition at low current efficiency. In the purification liberator cells, the copper content of the electrolyte is generally depleted to approximately 0.2 gram per liter. In the test cells it was possible to drop the copper content of the electrolyte to 10 grams per liter without appreciable loss in current efficiency. However, in commercial operations the decrease in current efficiency becomes noticeable at around 15 grams per liter. Below that concentration, the current efficiency decreases very rapidly. In lowering copper from 15 to 0.2 grams per liter, an overall current efficiency of 50 per cent is all that can be anticipated.

Generally anode current efficiency is greater than cathode current efficiency. This is manifested by a tendency for the copper content of the electrolyte to increase. Copper leached out in the treatment of the slime is frequently returned to the tank-room solution circuit and augments the increase. The amount of copper returned from the slime leach is from 0.05 to 0.21 per cent of the commercial cathode copper deposited. Means must be taken to remove the added copper or counteract the increase by the use of liberator (insoluble anode) cells. The withdrawal for purification may take care of the excess copper. However, it is generally necessary to subject a portion of the solution in the main circuit to electrolysis in cells employing antimonial lead anodes. In this manner, the copper content is depleted sufficiently to offset the increase in the soluble anode cells. The depletion is not carried to the point where there is danger of lowering the purity or quality of the copper deposited. Liberator cathodes, excepting those from some of the purification liberator cells, are suitable for production of wirebars. The average voltage of the liberator cells is approximately 1.9 volts, which means that the power required in producing liberator copper is approximately eight times that required in soluble anode cells. Hence, excess anode current efficiency contributes to excess power consumption.

Based on data from the larger refineries, the percentage of liberator copper produced (not including purification liberator copper) is from 0.04 to 1.75 per cent of the total good copper production. The amount of liberator copper produced plus the copper in the liquor withdrawn for purification, less the copper leached from the slime, measures the excess of anode over cathode current efficiency. The factors that contribute to the excess anode current efficiency are cuprous oxide in the anode and chemical oxidation of electrode copper or cuprous ion.

Copper from cuprous oxide enters the electrolyte without involving the transfer of any electrons to the anode. It is generally estimated that the copper entering solution from this source is half of the copper in the cuprous oxide, or approximately four times the oxygen content of the anode.

Impurities which enter solution by electrochemical oxidation lower the anode current efficiency and tend to decrease the excess copper dissolved by the amount of their equivalent weight. This counteracts the effect of cuprous oxide to some extent. The effect can be estimated from the impurity contents of the anode.

As previously mentioned, oxygen in the solution tends to increase anode current efficiency and decrease cathode current efficiency. Either result contributes to the excess of copper dissolved. Whether the oxygen reacts directly with copper in the electrodes or with Cu^+ ion the results are identical. If Fe^{+++} ion reacts as a chemical oxidizing agent during electrolysis with soluble anodes, the reactions would be similar to those of oxygen. The excess copper dissolved by chemical oxidation can only be estimated from the total excess copper dissolved minus the net result of the other two factors.

The following breakdown is based on data from eight of the major copper refineries:

Due to	Percentage of excess copper dissolved to total good cathode deposition	
	Minimum	*Maximum*
Cu_2O in anode	+0.28	+1.03
Impurities in anode	− .64	− .03
Chemical oxidation	+ .31	+ .85
Net	+ .20	+1.67

The total minimum or maximum is not the sum of the minima or maxima for various items, since neither all the minima nor all the maxima occur at the same refinery.

In all probability, the maximum and minimum shown above are exceeded for short periods during actual operations in many tank rooms.

Half of the amounts shown for chemical oxidation may be taken as an indication of the effect of oxygen on cathode current efficiency. Taking into consideration the test results, it is probable that the loss of cathode current efficiency due to chemical oxidation is somewhat higher than the preceding figures would indicate.

In recapitulation, the following probabilities appear to obtain under average normal operating conditions in the production of commercial cathode copper:

Cathode current efficiency loss due to short circuits, 2.0 to 10.0 per cent.

Cathode current efficiency loss due to stray current, 2.0 to 3.0 per cent.

Cathode current efficiency loss due to chemical oxidation, 0.25 to 0.75 per cent.

The anode current efficiency is from 0.20 to 1.70 per cent higher than the cathode current efficiency.

Current efficiency is only one item in the cost of electrolytic refining and comparisons of results from various refineries have little or no significance. Impurity problems and unit power and labor cost are entirely different. Low current efficiency may not necessarily mean high power or overall cost. Satisfactory elimination of impurities must be effected even if it means some sacrifice of current efficiency.

Cell Voltage

There has been considerable doubt as to the practical value of figures for cell voltages based on theoretical considerations or small-scale tests. In actual operation, factors such as irregularities in the thickness and surfaces of the electrodes, short circuits, passive anodes, dirty contacts, and irregularities in the circulation of the electrolyte influence cell voltage and cannot be definitely evaluated. However, these are factors that contribute to unsatisfactory results and hence the departures from normal cell voltage can be and are generally taken as indications of undesirable conditions. The general practice in connection with the tank-room control is to keep comprehensive statistical data on cell (or section) voltages and operating conditions. Experienced supervisors usually know how to correlate these data, but there are several components of cell voltage and for some of these there are many influencing factors. Hence, the relationships between cause and effect are extremely complex and not fully revealed or explained, except in generalities, by operating field data or statistics. Many significant changes have been based on laboratory investigations of cell voltage phenomena.

Several noteworthy investigations of cell voltage have been published[20]. Data from some of these will be used in this discussion. In addition, reference will be made to some unpublished data based on private communications from S. Skowronski[7] and the Central Research Laboratory of the American Smelting & Refining Co.[17] The latter organization has conducted extensive tests on cell voltage with equipment especially designed for this purpose. The tests have been made on both commercial and synthetic electrolytes. It has not been the primary purpose of most investigations to give a 100 per cent analysis of cell voltage components that would check with the total cell voltage found in commercial operations. There will always remain undeterminable differentials, although in data from Skowronski which will be presented, the differentials were surprisingly small. The investigations have generally been concerned with the relative effect of various factors on the components of cell voltage. Even semiquantitative relationships, which are consistent with field observations, have greater significance than vague generalities, and should be of more value in forecasting the result of contemplated changes in operating conditions.

The cell voltage proper may be divided into the following components: the IR drop through the electrodes and contacts; the IR drop through the electrolyte; the anode and cathode potentials. The effects of passive anodes, short circuits, etc., are not determined in test cells, nor can they be definitely correlated to operating factors such as temperature or composition of the electrolyte.

The IR drop through the electrodes and contacts can be determined only by actual tests. It depends on the electrode arrangement, weight of electrode, type and condition of contacts, and current density. It is a direct function of current density and ohmic resistance. In the multiple system, Walker arrangement, the total resistance in this category consists of the following items:

Conductor resistance of:
(*a*) Anodes
(*b*) Cathodes
(*c*) Cathode loops
(*d*) Cathode suspension bars
(*e*) Distributor bar

Contact resistance between:
(*f*) Distributor bar and anodes
(*g*) Cathodes and loops
(*h*) Loops and suspension bars
(*i*) Suspension bars and distributor bar

In the Whitehead arrangement the same items exist with the exception of (*e*), (*f*), and (*i*). In place of the latter two contacts there are single contacts between the suspension bars and anodes. The results of field tests, adjusted to current density of 18 amp. per sq. ft., indicate values for the IR drop through electrodes and contacts of 30 to 60 mv for the Walker system and 25 to 55 mv for the Whitehead system.

The IR drop through leads and bus bars is from 4 to 8 per cent of the total circuit voltage.

In the Nichols series system the resistance through the electrodes is negligible, and the only contacts and suspension or transfer bars are those involved in the support of the first and last rows of electrodes in each tank. The IR drop through these might be considered in the category of lead and bus-bar voltage, since the bars mentioned serve to conduct current to and from the entire 102 cells in the tank. The entire IR drop through electrodes and contacts is probably less than 1 mv per cell.

The IR drop through the electrolyte depends upon the current density, the resistivity of the electrolyte, and the electrode spacing. Based on a comprehensive investigation of the factors involved in the resistivity of normal tank-room electrolytes, Skowronski and Reinoso[20] state that the resistivity of any tank-house electrolyte may be calculated from its analysis. As illustrations they present the detailed calculation of resistivity for three different electrolytes. The calculated resistivities are compared with those which they obtained for the same electrolytes by the Kohlrausch method, and are found to check within 1 per cent.

Formulas are presented for the calculation of percentage resistivity relative to that of any solution of H_2SO_4, where the concentration is within the limits of normal refinery practice.

Percentage resistivity due to copper $= 100 + 0.657$ A. (A $=$ g/liter Cu)
Percentage resistivity due to nickel $= 100 + 0.760$ B. (B $=$ g/liter Ni)
Percentage resistivity due to iron $= 100 + 0.818$ C. (C $=$ g/liter Fe)
Percentage resistivity due to arsenic $= 100 + 0.0725$ D. (D $=$ g/liter As)

The total percentage resistivity for any combination of the four metallic ingredients of the electrolyte is calculated by multiplying the four individual percentages together. This total percentage resistivity, multiplied by the resistivity of a solution of any given acid concentration, will give the resistivity of an electrolyte of content equal to the values used for the metals and acids.

A table is presented showing the resistivity at 55°C (131°F) of H_2SO_4 at varying concentrations. The curve shown in Figure 8-9 is based on the authors' tabulation.

The authors explain that a correction must be made for arsenic (which is present as arsenic acid) in any calculation involving the resistivity of mixed acids, since both arsenic and sulfuric acids are titrated and reported together as free sulfuric acid in the usual method of determining acid. The actual grams of free acid present per liter can be found by subtracting 0.66 times the grams of arsenic present per liter from the grams per liter total free acid as found by titration.

Based on their deductions the authors state that if the resistivity of a normal electrolyte be determined at one temperature, it may be calculated at any other. Figure 8-10 shows the percentage resistivity of any H_2SO_4 solution at various temperatures based on its resistivity at 55°C as 100 per cent. The curve is based on data tabulated by the authors. For example:

Assume an electrolyte of the following composition and at 60°C: Total acidity as titrated = 200.0 g/liter; copper = 42.5 g/liter; nickel = 14.5 g/liter; iron = 0.7 g/liter; arsenic = 3.8 g/liter. By use of the equations and curves of Skowronski and Reinoso[20], the resistivity of this electrolyte is found to be 0.606 ohm per inch cube.

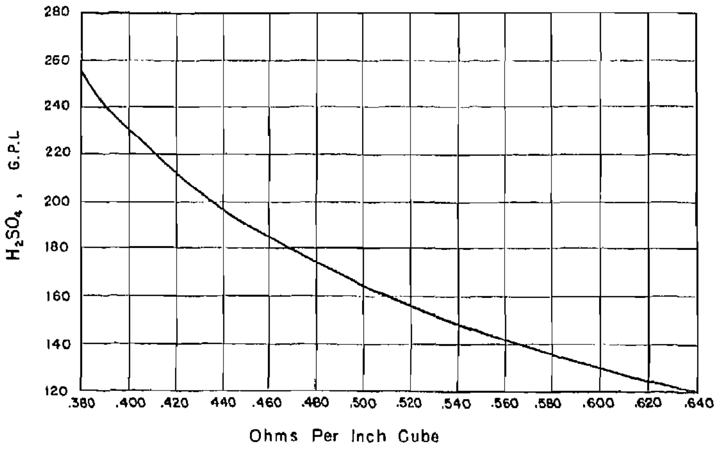


FIGURE 8-9. Resistivity of sulfuric acid at 55°C.

Consider a multiple cell, employing 700-pound anodes, 36 by 36 by 1¾ inches, at a spacing of 4¼ inches, and operating at a current density of 18 amp per sq ft. The average distance from anode surface to cathode surface, assuming two crops of cathodes, would be approximately 1.43 inches. The IR drop through the electrolyte would be $\frac{18}{144} \times 1.43 \times 0.606$ volt = 0.109 volt, or 109 millivolts.

Data from four different sources will be presented in regard to electrode potentials. Some adjustments must be made in the data presented in order to put the results on a comparative basis. In tests made with the Haring cell, the electrode potentials are not directly determined. However, in order to simplify the discussion and comparisons, the difference in electrode potentials and the influence of variables thereon will be stressed. This difference is the component of cell voltage that is the net result of the single potentials.

$E_D = E_A - E_C = (E_{AS} + P_A) - (E_{CS} - P_C)$, where

E_D = the difference in the dynamic electrode potentials,
E_A and E_C = the dynamic anode and cathode potentials,
E_{AS} and E_{CS} = the static anode and cathode potentials,
P_A and P_C = the anode and cathode polarizations.

Both the static electrode potentials and the electrode polarizations are affected by changes in certain conditions. Even though the anode and cathode are of like material, the anode and cathode polarizations are generally not affected to an equal degree. However, when they are of like material the changes in static potentials are equal, and the change in E_D is the sum of the changes in anode and cathode polarizations. In the Haring cell tests, anodes and cathodes of like material were used, and anode and cathode polarizations were the only results determined directly.

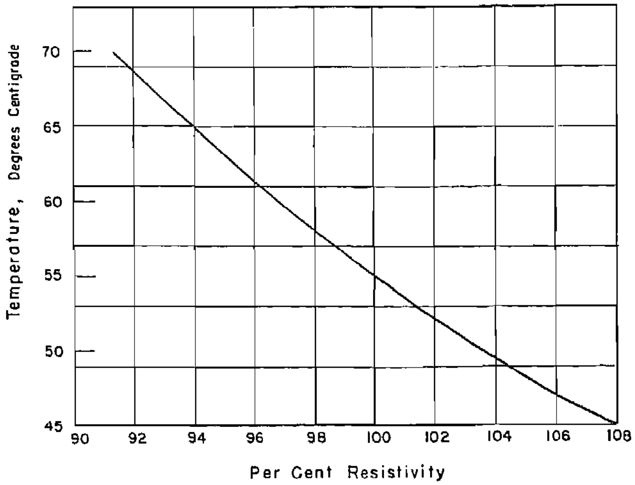


FIGURE 8-10. Variation of resistivity of sulfuric acid with temperature, expressed as percentage of the resistivity at 55°C.

Kern and Rowen[20] used cathodes of starting sheet copper, and three types of cast anodes, high purity, 99.13 per cent copper and 98.99 per cent copper. They found the effect on E_D due to the difference in purity and structure of the anode and cathode to be from 6 to 9 mv. This includes the effect of the film of slime. From other laboratory tests and field observations it is believed that a value of 10 mv is a fair estimate of the average component of cell voltage due to the difference in anode and cathode composition and structure. This voltage includes the effect of the slime film.

From the electrode potential curves based on data from the Central Research Division of the American Smelting & Refining Co., values of E_D can be found by subtracting the cathode potentials from the corresponding anode potentials (see Figure 8-11).

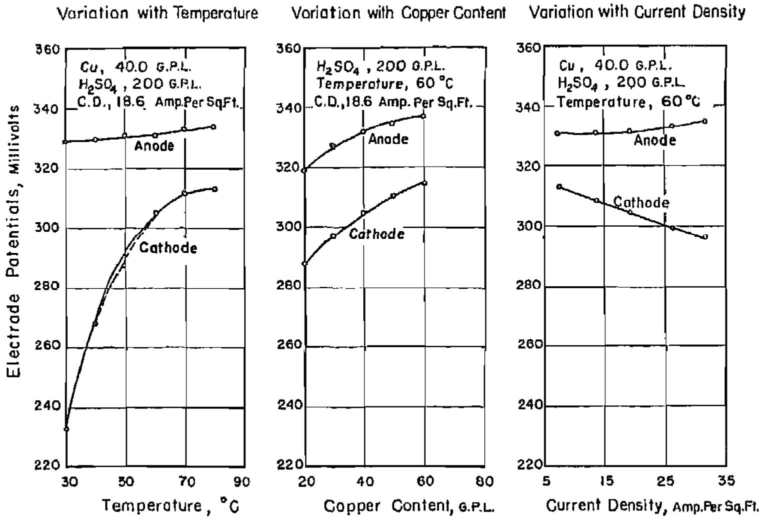


FIGURE 8-11. Copper electrode potentials. (Sheet copper electrodes, with no glue or other addition agent). (Central Research Division, American Smelting & Refining Company.)

Within the range of normal refinery conditions, the effects of certain factors on E_D are approximately as follows:

Effect of current density on E_D at 45 g/liter Cu and 60°C (140°F) temperature of electrolyte.

Central Research[17] of A. S. & R. Co.: 0.85 mv increase in E_D per amp per sq ft increase in current density.
Skowronski[7]: 0.78 mv increase in E_D per amp per sq ft increase in current density.

Effect of copper on E_D at 60°C (140°F) and 18 amp per sq ft current density.

Central Research[17] of A. S. & R. Co.....0.20 mv decrease in E_D per g/liter Cu increase.
Rouse and Aubel[20]..0.27 mv decrease in E_D per g/liter Cu increase.

Effect of temperature of electrolyte on E_D at 45 g/liter Cu and 18 amp per sq ft current density.

	Decrease in E_D per degree Centigrade increase in temperature				
Ranges	45 to 50°C	50 to 55°C	55 to 60°C	60 to 65°C	65 to 70°C

Central Research[17] of A. S. & R. Co.	2.1 mv	1.6 mv	1.5 mv	0.8 mv	0.3 mv
Rouse and Aubel[20]	2.4 mv	1.4 mv	.6 mv	.4 mv	—

The effect of the free acid and metallic impurities in the electrolyte is negligible.

Under the conditions of current density, 18 amp. per sq ft; H_2SO_4, 200 g/liter; Cu, 42.5 g/liter; temperature, 60°C; no glue or other addition agents, the difference in anode and cathode potential has a probable value of 36 mv, including an allowance of 10 mv for the effect of the difference in anode and cathode content and structure.

The effect of glue on polarization generally far exceeds that of any of the other items, such as temperature, H_2SO_4 and Cu content, and current density, and frequently the total amount of polarization due to glue exceeds that due to all other causes combined (see Figure 8-12).

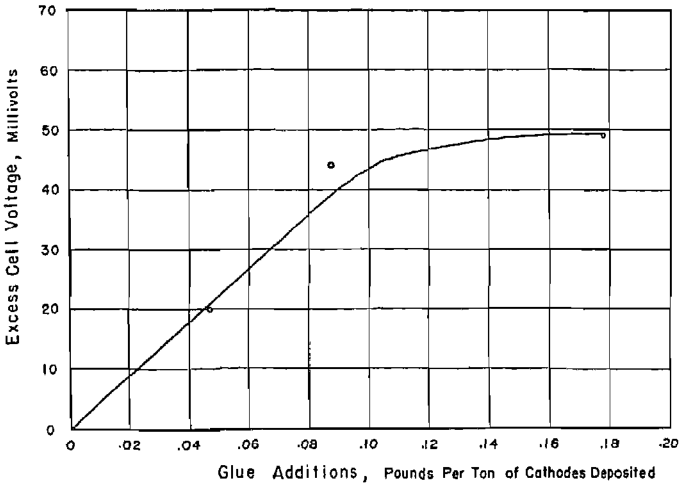


FIGURE 8-12. Effect of glue on cell voltage.

Cell voltage increases with rate of addition of glue, principally through increase in cathode polarization. Within the range of normal copper refining practice, the rate of increase is not affected materially by other conditions, such as temperature, content of electrolyte, or current density. (Data furnished by S. Skowronski.)

Glue affects the cathode potential only. All investigators agree on this and also that glue added to the electrolyte loses its effect on aging, whether the electrolyte is under current or not. For this reason the effect of glue on cell voltage cannot be evaluated except on the basis of glue added per unit of copper deposited.

The following data were furnished by Skowronski[7]. (All glue added in one addition):

Amount of glue, pounds per ton of copper deposited (24-hour basis)	0.0444	0.0888	0.1776
Maximum excess voltage indicated	54 mv	66 mv	71 mv
Excess voltage reduced to zero in	14 hr	16 hr	20 hr

When glue was trickled in over the 24-hour period, the results were as follows:

Amount of glue, pounds per ton of copper deposited	0.0444	0.0888	0.1776
Average excess voltage for 24-hour period	20 mv	42 mv	49 mv

It appears that the cell voltage increases at the rate of approximately 4.5 mv per 0.01 pound of glue per ton of copper deposited up to the addition of approximately 0.11 pound of glue per ton of copper. After that the glue appears to have reached a maximum effect (see Figure 8-12).

Tests were also conducted to determine the effect of current density on the excess voltage due to glue. It was found that current density had no effect whatsoever in increasing or decreasing the voltage caused by the glue addition.

According to Yu-lin Yao[11], chlorine up to 15 mg per liter increased the cathode polarization, which reached a maximum of 15 mv. Beyond that point additional chlorine reduced polarization. Rouse and Aubel confirm the reduction only, showing a decrease in cell voltage of 7 mv with increase of Cl content from 10 to 35 mg per liter.

Goulac alone has a very slight effect in decreasing cathode potential and hence increasing cell voltage, but when added with glue it appears to modify the effect of the glue on the cathode potential.

Purification of Electrolyte

There are two general schemes of purifying electrolyte. The first consists of the removal of copper, arsenic, and antimony by electrolysis in liberator tanks, followed by concentration of the liquor for the removal of nickel, iron, zinc, etc. The second is essentially the same except that the electrolysis in liberator tanks is preceded by the removal of part of the copper by concentration and crystallization. In the second scheme, the free acid may or may not be neutralized by shot copper in connection with the preliminary concentration.

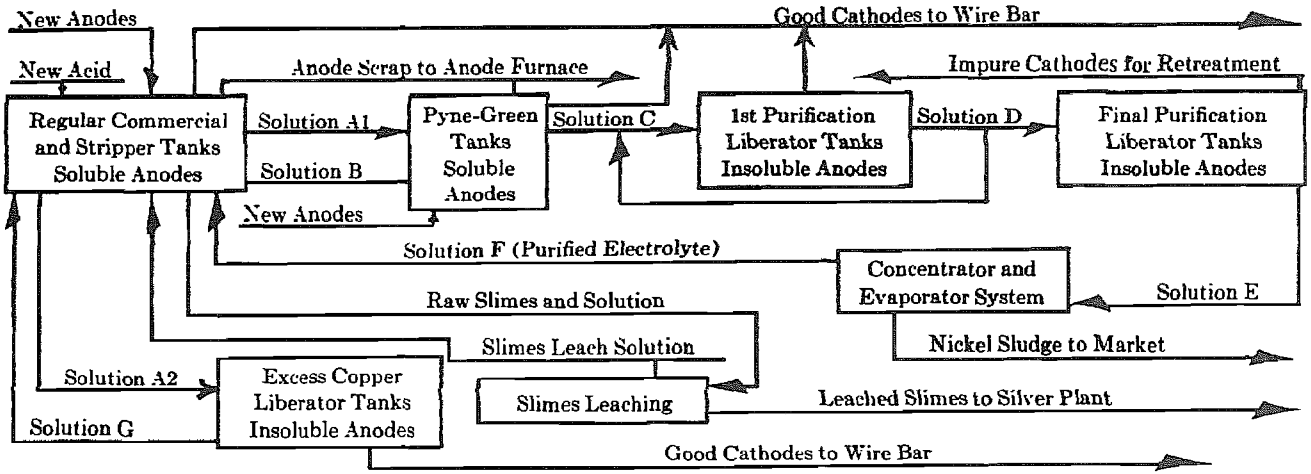
The removal of copper from impure electrolyte by cementation on scrap iron is actually not a method of purification, since no attempt is made to recover acid or by-products other than copper. It is seldom practiced except as an auxiliary method.

In either of the two general schemes the process may be modified or expanded and the details of procedure may vary, but the basic principles are the same. The copper is removed. This makes possible the removal of arsenic and antimony by electrolysis, and the recovery of nickel in a marketable form. Incidentally it does take some of the burden off the liberator tanks which are required for the removal of excess copper. The amount of any of the soluble impurities that must be removed is fixed by the amount introduced from the anode. The amount of solution withdrawn for purification is fixed by the allowable concentration of the major impurity in the electrolyte. Considering complete removal of this impurity from the electrolyte treated, the volume treated multiplied by the allowable concentration per unit volume must equal the amount of the impurity entering solution. The general practice is to remove as nearly as possible all of the major impurity in a single cycle of treatment. It may not be necessary to remove other impurities completely if the net amount removed in the cycle balances the input to the electrolyte at a satisfactory content thereof. Iron, zinc, etc., are completely removed with the removal of nickel and are generally relatively small in proportion thereto. The amount of antimony accumulating in the electrolyte is limited by its solubility. Hence, the only soluble metals that generally influence the details of procedure are nickel and arsenic. A few examples showing the disposition of the impurities will be given. These will be based on the flow sheets shown as Scheme No. 1 and No. 2. The examples are hypothetical but are in accord with results that have been obtained in actual operations (see pages 206-210).

The first step in Scheme No. 1 is electrolysis in Pyne-Green[21] tanks. Soluble anodes are employed in these tanks, and solution is withdrawn at both top and bottom outlets simultaneously. This procedure permits stratification of the electrolyte, the overflow solution being lower in copper and somewhat higher in free acid and impurities than the underflow. Thus the ratio of impurities to copper is increased in the overflow solution. This decreases the amount of copper that must be removed in the liberator tanks. The result is accomplished without the use of any appreciable amount of excess power. Cathodes of commercial quality are produced.

The overflow from the Pyne-Green tanks enters a solution circuit that is treated in the first or preliminary purification liberator tanks for further depletion of copper. Generally cathodes of commercial quality are produced in the preliminary liberators and at a current efficiency practically equal to that in the soluble anode tanks. The extent to which the copper is depleted in the first two steps depends on the arsenic content of the solution, since the lower the arsenic content the further the depletion of copper can be carried without danger of serious contamination of the cathode. The overflow from the Pyne-Green tanks will generally vary from 20 to 15 grams of copper per liter and the withdrawal

FLOW SHEET — PURIFICATION SCHEME NO. 1


New Anodes
New Acid
Regular Commercial and Stripper Tanks Soluble Anodes
Solution A1
Solution B
New Anodes
Anode Scrap to Anode Furnace
Pyne-Green Tanks Soluble Anodes
Solution C
1st Purification Liberator Tanks Insoluble Anodes
Solution D
Final Purification Liberator Tanks Insoluble Anodes
Good Cathodes to Wire Bar
Impure Cathodes for Retreatment
Solution F (Purified Electrolyte)
Concentrator and Evaporator System
Solution E
Nickel Sludge to Market
Raw Slimes and Solution
Slimes Leach Solution
Slimes Leaching
Leached Slimes to Silver Plant
Solution A2
Solution G
Excess Copper Liberator Tanks Insoluble Anodes
Good Cathodes to Wire Bar

A1 = Withdrawal to Pyne-Green tanks, preliminary to purification. A2 = Electrolyte to copper liberators for partial depletion of excess copper.
NOTE: A1 and A2 are of the same content and representative of electrolyte in commercial systems. A2 and G are equal in volume.
B = Underflow from Pyne-Green tanks. C = *Overflow from Pyne-Green tanks.* D = *Withdrawal to depositing out* (final purification liberators).
E = Decopperized solution. F = Purified acid for return to main system. G = Partially decopperized solution to main system.
NOTE: Depending on system of leaching, the slimes leach liquor may have to be treated by passing through copper sheets or scrap copper at boiling temperature for cementation of selenium and tellurium before return to main solution circuit. It is slightly higher in copper than normal electrolyte and contributes to excess copper dissolved.

The following tables show the relative volumes and contents of the solutions involved in the flow sheet for Scheme No. 1. They also show a balance for copper, acid, and the principal soluble impurities corresponding to the production of 100 tons of good cathodes. Volumes are expressed in cubic meters per 100 tons of cathodes (M^3 per $100T$). $1M^3=264$ gals. *The content of the anodes* treated is assumed to be:—Cu = 99.16%; Ag plus Au = 40.8 oz./ton; Se plus Te = 0.10%; Pb = 0.12%; Ni = 0.20%; As = 0.06%; Sb = 0.03%; Fe = 0.005%. The total excess copper dissolved from the anodes and slimes is assumed to be 0.95% of the good cathode production or 1,900 lb.

Sol.	M^3 per 100 T	Sp. Gr.	Grams per Liter					
			Cu	Free Acid	Ni	As	Sb	Fe
A_1	74.0	1.25	45.0	200	12.00	6.00	0.7	0.3
B	59.2	1.26	49.5	197	11.96	5.98	0.7	0.3
C	14.8	1.22	27.0	212	12.15	6.08	0.7	0.3
D	14.8	1.21	13.8	232	12.15	6.08	0.7	0.3
E	14.8	1.20	.2	254	12.15	3.50	0.4	0.3
F	3.2	1.61	—	1152	1.50	15.60	1.2	—
G	40.3	1.24	34.0	217	12.00	6.00	0.7	0.3

Materials	Pounds						
	Dry Weight	Cu	SO_4	Ni	As	Sb	Fe
New anodes	237,800	235,800	—	476	143	71	12
New 66°Bé acid	1,030	—	940	—	—	—	—
Total to process		235,800	940	476	143	71	12
Good cathodes							
Regular	196,990	196,950	—	3	2	2	0
Pyne-Green	1,600	1,600					
First purification liberator	433	433					
Excess copper liberator	977	977					
Impure cathodes	* 550	443	—	—	* 84	* 9	—
Anode scrap	35,650	35,350	—	72	22	11	2
Leached slimes	1,400	40	135	15	31	45	—
Nickel sludge	1,929	7	805	386	4	4	10
Total from process		235,800	940	476	143	71	12

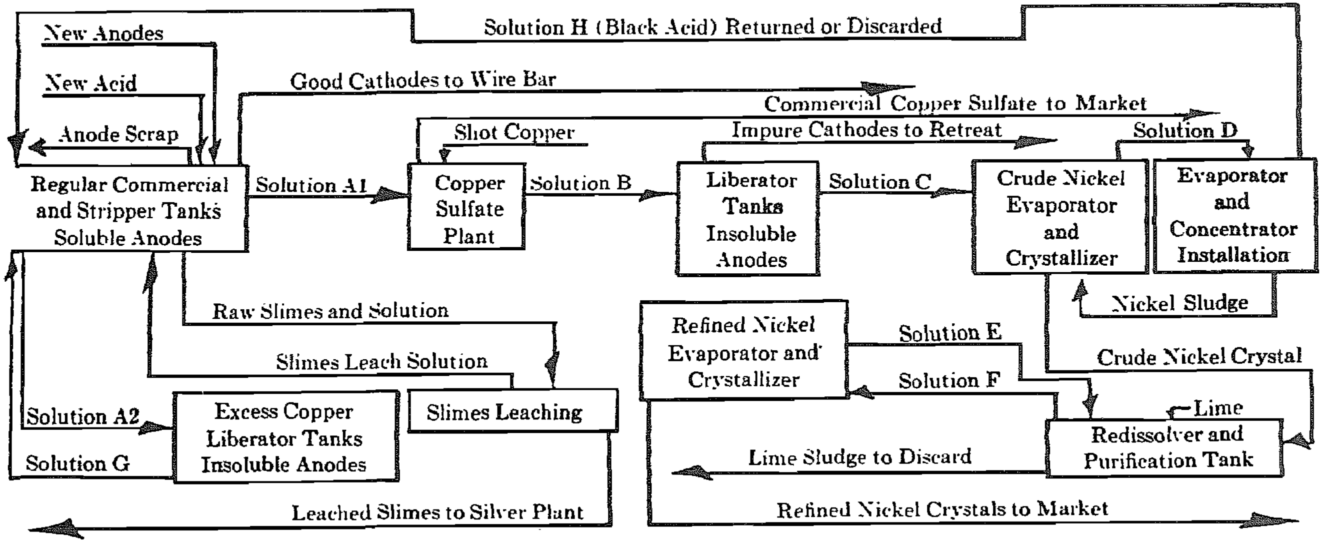
* These figures include As and Sb liberated as arsine and stibine.

The total good cathodes produced in the four categories is 200,000 lb or 100 tons.

The total liberator power required would be approximately 9.15% of the total deposition power not including lead and bus-bar losses, which should be relatively distributed.

The new 66° Bé commercial acid consumed is indicated to be 10.30 lb per ton of good cathode. Handling losses would probably increase this figure slightly.

FLOW SHEET — PURIFICATION SCHEME NO. 2


New Anodes
New Acid
Anode Scrap
Solution H (Black Acid) Returned or Discarded
Good Cathodes to Wire Bar
Commercial Copper Sulfate to Market
Shot Copper
Impure Cathodes to Retreat
Solution D
Regular Commercial and Stripper Tanks Soluble Anodes
Solution A1
Copper Sulfate Plant
Solution B
Liberator Tanks Insoluble Anodes
Solution C
Crude Nickel Evaporator and Crystallizer
Evaporator and Concentrator Installation
Nickel Sludge
Raw Slimes and Solution
Refined Nickel Evaporator and Crystallizer
Solution E
Crude Nickel Crystal
Slimes Leach Solution
Solution F
Lime
Solution A2
Excess Copper Liberator Tanks Insoluble Anodes
Slimes Leaching
Redissolver and Purification Tank
Solution G
Lime Sludge to Discard
Leached Slimes to Silver Plant
Refined Nickel Crystals to Market

For solutions A1, A2, and G, see Flow Sheet for Scheme No. 1.
B = Last copper sulfate mother liquor. C = Decopperized mother liquor to nickel plant. D = Crude nickel mother liquor.
E = Refined nickel mother liquor. F = Purified nickel liquor. H = "Black Acid" recovered from concentration of crude nickel mother liquor.
It may be returned to main system or discarded, depending on the extent to which arsenic and antimony are removed in the liberator tanks.

The following tables apply to the Flow Sheet for Scheme No. 2, and are based on treatment of anodes of the same content as Scheme No. 1, and the same excess copper dissolved.

Sol.	Cubic Meters per 100 T	Sp. Gr.	Grams per Liter					
			Cu	Free Acid	Ni	As	Sb	Fe
A_1	14.7	1.25	45.0	200	12.0	6.0	0.7	0.3
B	2.4	1.28	36.9	25	67.9	38.3	1.15	1.1
C	2.4	1.26	.2	81	67.9	20.3	.45	1.1
D	1.0	1.30	.2	190	69.6	20.9	.40	1.1
E	.3	1.24	—	—	70.0	—	—	trace
F	2.5	1.20	—	—	69.6	—	—	trace
G	16.6	1.25	34.0	217	12.0	6.0	.7	.3
H	.2	1.62	—	950	1.5	240.0	1.25	—

Materials	Pounds						
	Dry Weight	Cu	SO_4	Ni	As	Sb	Fe
New anodes	239,031	236,985	—	478	143	71	12
New acid	9,786	—	8,937	—	—	—	—
Shot copper	4,160	4,117	—	—	—	—	2
Total to process		241,102	8,937	478	143	71	14
Good cathodes							
Regular	199,598	199,558	—	3	2	2	0
Excess copper liberator	402	402					
Impure cathodes	* 300	194	—	—	* 87	* 3	—
Anode scrap	35,834	35,527	—	72	22	11	2
Leached slimes	1,405	40	136	15	31	45	—
Copper sulfate	21,087	5,324	8,095	30	—	—	6
Refined nickel sulfate	1,541	—	566	344	—	—	—
Lime sludge	90	1	55	14	1	2	6
Copper sulfate refuse	—	56	85	—	—	8	—
Total from process		241,102	8,937	478	143	71	14

* These figures include As and Sb liberated as arsine and stibine.

The total good cathode produced in the two categories is 200,000 lb or 100 tons.

The total liberator power required would be approximately 3.50% of the total deposition power not including lead and bus-bar losses, which should be relatively distributed.

The new 66° Bé commercial acid consumed is indicated to be 97.86 lb per ton of cathodes produced, but as compared with Scheme No. 1, there is an extra credit equivalent to 88.64 lb of acid per ton of cathodes recovered in the form of copper sulfate. On this basis the comparative consumption would be 9.22 lb per ton of cathodes. With discard of black acid, which would probably be the case in Scheme No. 2, the net consumption would be 10.24 lb per ton, which is almost identical with Scheme No. 1.

Note that on account of a relatively greater withdrawal of electrolyte than required for Scheme No. 1, the anodes required to produce 100 tons of cathode are slightly increased.

from the first liberators from 15 to 8 grams of copper per liter. Solution is withdrawn from the first liberator circuit and is passed through the final set of liberators in cascade. Here the copper is depleted to approximately 0.2 gram per liter. The extent to which the arsenic is removed depends on the requirement. The ratio in which arsenic is removed depends on the ratio of arsenic to copper after the latter has been depleted to approximately 8 grams per liter. The final liberators should be hooded or operated out-of-doors, since a portion of the arsenic is liberated as arsine.

The decopperized solution is generally concentrated in vacuum or direct-fired evaporators, or both, doing the preliminary concentration in vacuum evaporators. The final concentration is carried to 55 to 62°Bé. This concentration removes practically all of the nickel, iron, and zinc and small amounts of arsenic and antimony in the form of a sludge. This sludge may be marketed or further treated for the production of a purified nickel product. The final solution product, called "black acid," is marketed, returned to the main solution circuit, utilized in other operations, or discarded. The accumulation of Na, K, Mg, and Al in the black acid will generally necessitate the discard or marketing of a portion thereof, since these metals can only be eliminated by distillation.

Scheme No. 1 may be modified by the elimination of the Pyne-Green tanks, or by the elimination of these tanks and the first purification liberators. In the latter case, total soluble impurities are usually low.

Scheme No. 2, as shown in the flow sheet, contemplates production of high-quality copper and nickel sulfates. Neutralization with copper of the free acid in the normal electrolyte will result in practically complete saturation at 100°C. Thus very little evaporation is required prior to the first crystallization. Copper sulfate is separated from the other metal sulfates by fractional crystallization in two or more stages. Details of procedure depend on the purity of copper sulfate desired and the amount of impurity in the electrolyte. Complete separation of copper and other metals is not obtained by crystallization and so the last mother liquor is treated in liberator tanks. After removal of the copper and of the required amount of arsenic and antimony, a crude nickel sulfate is produced by concentration and crystallization. The crude nickel crystals are redissolved. The nickel solution is purified by treatment with lime, and refined nickel sulfate is produced by concentration and crystallization from the purified liquor. The crude nickel liquor may be treated for the production of nickel sludge and black acid as in scheme No. 1. In this case, the nickel sludge is redissolved and returned to the crude-nickel solution circuit.

In a modification of this process[10] the free acid in the electrolyte is not neutralized prior to the production of copper sulfate. This modification is usually adopted when the amount of nickel is relatively low and the arsenic high. A mother liquor of approximately 15 grams of copper per liter and relatively high in arsenic would be produced. This can be efficiently treated for the removal of copper and arsenic in liberators.

Power Conversion and Distribution

Copper refining requires a constant source of direct current[22] of fairly low voltage (about 150) and high amperage (up to 20,000). To obtain the high amperage, the direct-current producing units are normally connected in parallel.

Most refineries purchase A.C. and convert to D.C. Some refineries generate their own A.C. power, using steam turbines or Diesel engines, and Raritan is now using a Diesel to drive a D.C. generator. For converting A.C. to D.C. four main types of equipment are used: motor-generator sets, rotary converters, mercury-arc rectifiers, and mechanical rectifiers. Selenium rectifiers, because of their low efficiency (65-80 per cent), are not used for copper refining, except for experimental work.

Motor-generator sets are most commonly used because of their great flexibility. Although several small motor-generator sets cost more than one equivalent large set, smaller sets give better opportunity for maintenance without shutdown of the complete installation. For this reason they are preferred to large sets.

Motor-generator sets cost about as much as mercury-arc rectifiers and slightly more than rotary converters. Especially when separate excitation is employed, motor-generator sets can be used over a wide operating voltage range such as is encountered when many tank-house sections are cut out of circuit because of lack of copper to refine. Motor-generator sets require very little maintenance. Provided it is operated near its maximum rating, the motor-generator set has an efficiency of 85 to 88 per cent.

Although at about 350 volts the mercury-arc rectifier has the same over-all efficiency as a motor-generator set, at 150 volts it has an efficiency of only 82 per cent compared to 88 per cent for a motor-generator set of the same ampere rating. While the mercury-arc rectifier is almost universally used for high-voltage applications, such as aluminum reduction, it is used at only two copper refineries, at Cerro de Pasco (a 400-volt, 6,500-ampere unit) and at Bolidens (a 250-volt, 6,000-ampere unit). At Cerro de Pasco the cell voltage is 0.46 volt due to 7-inch electrode spacing, necessitated by using blister copper anodes. Bolidens has a

0.3 to 0.35 cell voltage. Other copper refinery cells have a voltage drop of only 0.2 to 0.25. The high voltage drops at Cerro and Bolidens explain the choice of the mercury arc rectifiers at these plants. The voltage drop through a mercury-arc rectifier is about 14 to 15 volts, which is a distinct disadvantage except on high-voltage applications (250 volts and up).

Several of the older refineries still use rotary converters. Although their efficiency is higher and their cost lower than either motor-generator sets or mercury-arc rectifiers, their maintenance cost is higher and their flexibility less than the motor-generator sets. Also, the cost of the auxiliary switching gear and transformer actually makes the rotary converter more expensive than the motor-generator set.

The mechanical rectifier has some advantages, but its first cost and maintenance of contacts are high, especially with variation in A.C. line frequency or voltage. The voltage drop through mechanical rectifiers is 3 to 4 volts. This rectifier made its appearance in Germany in 1940. Because of the War, few installations of this type of rectifier have been made to date. Its efficiency is much higher than any other D.C. unit. The first large mechanical rectifier (a 1,500-kw unit) for a copper refinery was installed in 1952 at the U.S. Metals Refining Co. at Carteret, N. J. Its performance will no doubt be followed with much interest by other refineries.

To summarize, at the present time motor-generator sets are most ideally suited for the direct-current requirements for most electrolytic copper refineries. Where high-voltage circuits may be employed, the mercury-arc rectifier deserves consideration.

For comparison, the December, 1951, costs (in Canadian dollars) of D.C. generating equipment F.O.B. Montreal East, Quebec, are given below. The costs are for units of 675 kw rating, 135-12 volts, 5,000 amperes.

Type of D.C. unit	Approximate Cost	Cost Ratio
Motor-generator set	$55,000.	1.0
Mercury-arc rectifier	55,000.	1.0
Rotary converter*	50,000.	0.9
Mechanical rectifier	72,000.	1.3

* Without switchgear and transformer.

For additional comparison, the over-all efficiencies at various voltages of 5,000-ampere units are shown in Figure 8-13[23].

To reduce line losses as much as possible, the direct-current generating or converting equipment is located so that conductor lengths are a minimum. The conductors and bus bars are normally made of copper. While the bus bars at the cells are of solid cross section, the conductors from the powerhouse to the end cells in the circuit are built up of a series of smaller flat bars with air spaces between for cooling. Line losses are normally from 4 to 8 per cent of the total circuit voltage. The ampere loading of bus bars at the major copper refineries varies from 225 to 830 amperes per square inch.

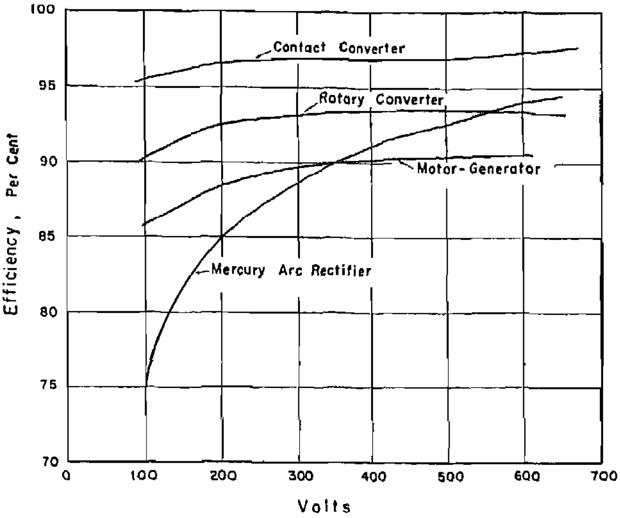


FIGURE 8-13. Comparison of efficiency as a function of voltage for various types of A.C.-D.C. conversion.

At a current efficiency of 93 per cent and a cell voltage of 220 mv, the net requirement of power for electrolytic copper refining would be 182 D.C. kw-hr per ton of copper deposited. In addition to this, power is required for liberator cells and auxiliary tank-room equipment, such as cranes and pumps. Furthermore, there are lead and bus-bar losses and conversion equipment losses, so that the total power requirement for a typical multiple tank room would be about 280 A.C. kw-hr per ton of copper deposited.

A breakdown of the power requirement is tabulated below:

	Kw-hr per ton	Per cent of total
Net deposition power	182	65.0
Liberator power	22	7.8
Lead and bus-bar losses	12	4.3
Total D.C. power	216	77.1
Conversion loss	38	13.6
Total A.C. power for deposition	254	90.7
Auxiliary equipment	26	9.3
Grand total A.C. power	280	100.0

TABLE 8-3. TANK-ROOM DATA

	American Smelting and Refining Co. Baltimore, Md.	American Smelting and Refining Co. Barber, N.J.	American Smelting and Refining Co. Tacoma, Wash.	Anaconda Copper Mining Co. Great Falls, Mont.	Bolidens Gruvaktiebolag Roonskar, Sweden	Canadian Copper Refiners Ltd. Montreal E., Que.		Cerro de Pasco Copper Corp. Oroya, Peru
Anodes						Domestic	Noranda	
Cu %	99.43	99.+	99.0	99.49	99.3	99.41	99.29	97.5 — 97.9
Ag oz/ton	18.7	55.	90.2	46.72	36.	46.00	32.54	160 — 250
Au oz/ton	1.41	1.5	3.59	.32	4.5	3.29	4.66	1.0 — 2.0
Se %	.061	.07	.051	.012	.2	.13	.14	.016
Te %	.045	.02	—	.024	—	.029	.026	.010
As %	.064	.10	.06	.059	.004	.012	.0007	.10
Sb %	.031	.10	.198	.027	.015	.075	.0001	.30 — .70
Bi %	.008	.002	.007	.003	.004	—	—	.01
Pb %	.031	.100	.073	.024	.05	.058	.006	.30 — .60
Ni %	.157	.200	.21	.028	.26	.02	.05	.025
Co %	—	—	—	—	—	—	—	—
Fe %	.0017	—	.071	.0028	.003	.0012	.0009	.02
S %	—	.005	.011	.0016	.015	.0063	.0061	.029
Sn %	—	—	—	—	—	—	—	—
Zn %	—	—	—	.0025	.015	—	—	.007
Insol. %	—	—	—	—	.003	—	—	—
O %	—	—	—	—	.25	—	—	.40 — .50
Length, inches	38	35.5	37.5	35.75	37.8	36		26
Width, inches	34.5	35.5	28	27.25	27.2	36		36
Thickness, inches	1.5625	1.875	1.50	1.625	1.50	1.50		1.625 — 3.0
Weight, lbs.	700	670	530	440	375	625		450 — 525
Type of suspension	Cast lugs	Cast lugs	Cast lugs	Cast lugs	Cast lugs	Cast lugs		Cast lugs
Spacing, cen. to cen., in.	3.875	4.25	4.0	3.75	4.75	4.0		7.0
Life, days	27	28	31	38	18	24		24
Scrap, %	18	16	18	16	20	14		18 — 20
Anode Slimes								
per ton anodes, lbs.	12.5	16.4	17	5.6	17	16		45
Removed after ? days	27	28	31	38	18 or 36	24		24
Starting Sheets								
Length, inches	41	36	38	36	39.75	37		30
Width, inches	37	37.5	29	28.5	28.4	37.5		36
Thickness, inches	.031	.025	.031	.025	.024	.023		.035
Weight, lbs.	10.5	10.5	11.5	7	7 — 9	13		11
Type of suspension	1 wide loop	1 wide loop	2 — 4″ loops	2 small loops	2 small loops	1 wide loop		2 small loops
Cathodes								
Life, days	13.5	14	15	19	9	8 — 12		8
Weight, lbs.	285 — 300	300	210	185	155	165 — 250		120
Method of washing	Dipping and spraying	Sprays on load. mach.	Sprays on load. mach.	Dipped in hot water	Dipped in hot water	Sprays in wash. mach.		Hot-water soak and spray
Wet Flapping ?	Yes	No	No	No	No	No		Yes
Inspection — day shift ?	Yes	Yes	Yes	Yes	Yes	Yes		Yes
Inspection — P.M. shift ?	No	No	Yes	New sheets only	Yes	New cath. only		Yes

	A. S. & R. Co. Baltimore	A. S. & R. Co. Barber	A. S. & R. Co. Tacoma	Anaconda Great Falls	Bolidens Sweden	C.C.R. Ltd. Montreal East	Cerro de Pasco Peru
Electrolyte							
Specific gravity	1.265	1.25	1.25	1.28	1.25	1.25	
Cu, g/liter	49.5	47.0	45.0	42.7	52	44.0	37 — 40
Free acid, g/liter	205	205.	215	185	170	190	125 — 135
As, g/liter	4.5	6.0	2.1	2.8	4	.9	1.5 — 2.6
Ni, g/liter	9.6	12.0	15.0	16.1	10	7.7	1.5 — 2.5
Fe, g/liter	.26	.2	.4	2.5	0.6	.5	5.0 — 7.0
Cl, g/liter	—	—	—	—	—	—	Zn .5 — .7
Sb or Bi, g/liter	Sb .43	Sb .7	Sb .65	Sb .52	0.35 Sb, 0.35 Bi	Sb .3	Sb .35 — .40
Temperature, cell inlet °C	60	61.1	62.8	55.0	62.2	65.6	55.0
Temperature, cell outlet °C	55.5	56.7	58.9	48.9	58.0	60.0	50.0
Circulation, gal. per min.	3.86	4.5	6.0	6.0	1.7	4.5	3.0
Type of pumps	Vert. centrifugal	Horiz. centrifugal		Pohle air lifts	Horiz. centrifugal	Horiz. centrifugal	Centrifugal
Heating equipment	Lead steam coils in solution tanks	Karbate tubular heat exchangers	Lead tubular Heat exchangers	Lead steam coils in solution tanks	Lead steam coils in solution tanks	Lead steam coils in solution tanks	Karbate heaters (steam)
Scheme of purification B.V.* =copper sulfate Lib.**=electrolytic liberation	Lib.** of Cu,As,Sb Removal of Ni,Fe, etc. by concentrn.	Segregation in Pyne-Green tanks Lib.** of Cu,As,Sb Removal of Ni,Fe, etc. by concentrn.	Lib.** of Cu,As,Sb Removal of Ni,Fe, etc. by concentrn.	B.V.* production by concentration Lib.** of Cu,As,Sb Removal of Ni,Fe, etc. by concentrn.	Lib.** of Cu,As,Sb Removal of Ni,Fe, etc. by concentrn.	B.V.* production by neut. and conc. Lib.** of Cu,As,Sb Removal of Ni,Fe, etc. by concentrn.	B.V.* production
Addition Agents							
Glue, lbs./ton cath.	.125	.113	.10	.0365	.10	.086	.65 — .70
Goulac, lbs./ton cath.	.625	.452	—	.096	.03	—	—
Others, lbs./ton cath.	HCl .5	NaCl .15	NaCl .13	NaCl .066 Casein .055	Thiourea .10	Avitone .071	HCl 2.00
Power							
Amperes per Cell	15,200	10,800	*8,600 — 10,300*	*5,385*	5,000 — 8,000	18,000	6,000 — 6,500
Cath. C.D., amps./sq. ft.	18.2	19.3	*16.0*	11.2	16 — 24	19.59	16.66 — 18.00
Cell voltage	.230	.230	.200	.250	0.30 — 0.35	.275	.46
Conversion equipment A.C. to D.C.	Syn. rotary converters	Steam turbine generators	M.G. sets	M.G. sets	M.G. sets and mercury-arc rectifier	M.G. sets	Mercury-arc rectifier
K.W. of generators	954	1,500 and 2,500	1,110	600	400	675	2,600
Amp. of generators	8,670	12,000 and 20,000	6,000	3,000	4,000	5,000	6,500
Maximum voltage of gen.	110	150 and 160	185	200	90	135	400
Current efficiency %	93.2	94.5	93.0	93 — 94	92	96	94 — 97
K.W. hrs./ton cath.	196	181	209	209	320 — 400	205	480
Lbs. cath./K.W. day	244	265	230	230	150 — 120	233	100
Electrolytic Cells							
Material	Concrete — wood	Concrete — wood	Concrete — wood	Wood	Concrete — wood	Monolithic concrete	Concrete
Lining	Lead	Lead	Lead	Antimonial Lead	Antimonial lead	Antimonial lead	Lead
Length	13′ 5″	11′ 2″	99″ — 147″ — 174″	10′ 3″	9′ 10″	16′ 7″	15′ 0″
Width	3′ 7″	3′ 6″	2′ 9″	2′ 10″	2′ 9.5″	3′ 7.5″	3′ 1″
Depth	4′ 1″	4′ 0″	3′ 10″	3′ 9″	4′ 1.25″	4′ 1.5″	4′ 6″
Anodes per cell	40	30	22 — 35 — 42	32	24	48	24
Cathodes per cell	41	31	23 — 36 — 43	33	25	49	25
System and arrangement	Whitehead	Whitehead	Whitehead	5-cell cascade 2 bus bars each	Walker	Whitehead	Walker
Amps./sq. in. bus bar	500	500	500	770	700 — 1,100	450	600 — 650
Electrolyte inlet to cell	Top	Top	Bottom	Top	Top	Bottom	Top

	Electrolytic Ref. & Smelting Co., Ltd. Port Kembla, N.S.W.		Inter. Nickel Co. of Canada, Ltd. Copper Cliff, Ont.	Kennecott Copper Corp. Garfield, Utah	Mt. Lyell Mining & Railway Co. Ltd. Queenstown, Tasmania	Mufulira Copper Mines, Ltd.	Norddeutsche Affinerie Hamburg, Germany	Outokumpu Oy. Pori, Finland
Anodes	Normal	High Test			Blister			
Cu %	99.32	98.50	99.18	99.40	99.20	99.65	98.9 — 99.1	99.0 — 99.3
Ag oz/ton	10.62	26.30	—	17.138	3.20	2.73	19.84 — 30.13	10.29
Au oz/ton	5.79	2.82	—	1.523	.62	.015	.42 — .64	.43
Se %	.022	.029	.05	.047	.015	.0014	.04 — .06	.017
Te %	.039	.025	.007	.022	.0058	—	.002 — .006	—
As %	.08	.220	.007	.062	.0026	—	.09 — .20	.008
Sb %	.104	.310	.0015	.023	.0047		.06 — .11	trace
Bi %	.004	.006	.001	.004	trace	.0015	.0033 — .0042	.002
Pb %	.039	.183	.006	.035	.009		.11 — .17	.0046
Ni %	.123	.251	.50	.075	.012	.0065	.24 — .34	.71
Co %	—	—	—	—	trace		—	.0004
Fe %	.009	.022	.0010	.014	.045		.03 — .10	.014
S %	—	—	—	.006	.14	.0066	—	.005
Sn %	—	—	—	—	—		.007 — .10	.0008
Zn %	—	—	—	—	trace		—	.0035
Insol. %	.05	.058	—	.046	.075		—	.002
O %	—	—	—	.22	—		.15	.18
Length, inches	31		36	39	36.75	36	34.625	36.50
Width, inches	34		36	35	27.50	36	26	35.50
Thickness, inches	1.50 — 1.75		1.375	1.625	2.75	1.25	1.344	1.50
Weight, lbs.	550 — 610		580	700	570	525	354	605
Type of suspension	Cast lugs		Cast lugs	Cast lugs	Loops	Cast lugs	Cast lugs	Cast lugs
Spacing, cen. to cen., in.	4.25		3.50	3.875	5.50	4.50	3.547	4.75
Life, days	42		28	27	18 — 25	28	25	21
Scrap, %	18		12.4	15	11 — 13		18	13 — 15
Anode Slimes								
per ton anodes, lbs.	20		8.3	15	35 — 40	2.55	12.1	9 — 13
Removed after ? days	42		28	27	18 — 25	28	25	21
Starting Sheets								
Length, inches	31		37	41	38	37.125	36.25	37
Width, inches	36		38	37	30	37	27.875	37
Thickness, inches	.02		.026	.025	.02	.025	.024	.025
Weight, lbs.	7		12	11.2	8	10.5	7.2	14
Type of suspension	2 small loops		2 small loops	1 wide loop	2 small loops	2 — 4″ loops	2 small loops	1 wide loop
Cathodes								
Life, days	14		13.7	13.5	3 — 6	14	12.5	7
Weight, lbs.	140 — 160		260	300	95 — 125	220	154	176
Method of washing	Dipping in hot water		Dip and hot-water spray	Dip in hot water and spraying	Dip in boiling water		Dipping in hot water	Soaking and spraying
Wet flapping ?	No		Yes	No	No		Yes	No
Inspection — day shift ?	Yes		Yes	Yes	Yes		Yes	Yes
Inspection — P.M. shift ?	No		New cath. only	No	Yes		No	Yes

	E. R. & S. Ltd. Port Kembla	Inco Copper Cliff	Kennecott Garfield	Mt. Lyell Queenstown	Mufulira N. Rhodesia	Norddeutsche Hamburg	Outokumpu Pori
Electrolyte							
Specific gravity	1.24	1.28	1.25	1.18 — 1.21	1.18 — 1.20	1.20	1.23
Cu, g/liter	45	39	42	40 — 45	40 — 50	30 — 35	37
Free acid, g/liter	170 — 190	203	200	135 — 155	200 — 125	168 — 180	200
As, g/liter	6 — 8	.54	7	.5 — 1.0		10 — 12	.4
Ni, g/liter	8 — 10	19.7	10	3 — 5		18 — 21	18
Fe, g/liter	3	.16	.5	3 — 4		.35	.5
Cl, g/liter	Zn .3 — .4				.035	.05	
Sb or Bi, g/liter	Sb .5 — .6	Na$_2$SO$_4$ 11.5					
Temperature, cell inlet °C	60	62.8 — 65.6		45 — 55	60 — 63	57.8	60
Temperature, cell outlet °C	54.4	58.3 — 61.1		35.6 — 46.1		55	56.7
Circulation, gal. per min.	4	2.5 — 3.0		4 — 5	3 — 4	3.2	4.5
Type of pumps	Vert. & horiz. cent.	Vert. centrifugal	Centrifugal	Centrifugal	Horiz. centrifugal	Centrifugal	Horiz. centrifugal
Heating equipment	Lead coils, Karbate heat exchangers	Lead steam coils in solution tanks	Karbate tubular heat exchangers	Lead steam coils in solution tanks		Steam coils	Lead tubular heat exchangers
Scheme of purification B.V.* =copper sulfate Lib.**=electrolytic liberation	B.V.* production	Segregation in Pyne-Green cells Lib.** of Cu,As,Sb Removal of Ni,Fe, etc. by concentrn.	Lib.** of Cu,As,Sb Removal of Ni,Fe, etc. by concentrn.	B.V.* production		Lib.** of Cu,As,Sb Removal of Ni,Fe, etc. by concentrn.	Lib.** of Cu,As,Sb Removal of Ni,Fe, etc. by concentrn.
Addition Agents							
Glue, lbs./ton cath.	.05	.15	.05	.25 — .30	.11	.012	.07 — .15
Goulac, lbs./ton cath.	—	.62	.25	Casein .5 — .75	.624	—	—
Others, lbs./ton cath.	Casein .05	NaCl .02		Sul. cast. oil .1 — .2	HCl .34	Oil .020	Thiourea .11
Power							
Amperes per cell	4,300 — 5,000	11,800	15,000	6,000 — 10,000	8,600	6,700	11,500
Cath. C.D. amps/sq. ft.	11.4 — 13.2	15.9	17.8	21 — 30	13.8	14.8	21.8
Cell voltage	.200 — .300	.232	.210	.400 — .450		.260	.290
Conversion equipment A.C. to D.C.	M.G. sets	M.G. sets	M.G. sets	M.G. sets	M.G. sets	Steam turbine generator	M.G. sets
K.W. of generator	750	960	1,000	800	1,000	1,050	815
Maximum voltage of gen.	145	160	125	80	120	150	45
Amp. of generator	5,000	6,000	8,000	10,000	10,000	7,000	14,000
Current efficiency %	90 — 92	96	95	92 — 94		91	94
K.W. hrs./ton cath.	280 — 300	192.7	175	402 — 446		201	254
Lbs. cath./K.W. day	190 — 168	249	275	120 — 108		239	188
Electrolytic Cells							
Material	Concrete — wood	Concrete	Concrete	Concrete	Concrete	Concrete	Concrete
Lining	Lead	Antimonial lead	Antimonial lead	Antimonial lead	Lead	Antimonial lead	Antimonial lead
Length	10′ — 9′ 3″	11′ 3″	13′ 7″	10′ 2″	12′ 6″	10′ 6″	11′ 10.5″
Width	3′ 6″ — 3′ 6″	3′ 6″	3′ 7″	2′ 8″	3′ 6″	2′ 8″	3′ 7.25″
Depth	4′ 0″ — 3′ 5″	3′ 9.5″	4′ 0″	3′ 9″	3′ 9″	4′ 1″	4′ 0″
Anodes per cell	24	38	40	21	32	33	28
Cathodes per cell	25	39	41	22	33	34	29
System and arrangement	Walker	Walker	Whitehead	5-cell cascade Double jumper bar	Walker	Walker	Whitehead
Amps./sq. in. bus bar	538 — 625	524	375	500 — 830	430	645	600
Electrolyte inlet to cell	Bottom	Bottom	Bottom	Top		Bottom	Top

	Phelps Dodge Refining Corp. El Paso, Texas	Phelps Dodge Refining Corp. Laurel Hill, N.Y.	Raritan Copper Works Perth Amboy, N.J.	Rhodesia Copper Refineries Ltd. N'Kana, N. Rhodesia	Societe General Metallurgique de Hoboken, Belgium	U.S. Metals Refining Co. Carteret, N.J.
Anodes						
Cu %	99.60	99.5	99.40	99.78	99.00	98.90
Ag oz/ton	5.0 — 20.0	6.0 — 10.0	8.673	2.37	40 — 60	46.18
Au oz/ton	.1 — .7	.25	.232	.018	.05 — .3	
Se %	.02	.02	.035	.0143	—	.044
Te %			.008	.0006	—	.018
As %	.003	.03	.038	.0018	.17	.03
Sb %	.001	.025	.024	.0003	.02	.05
Bi %	—	—	.002	.0061		—
Pb %	.01	.04	.045	—	.20	.21
Ni %	.03	.07	.043	.0161	.10	.22
Co %			—	.0055		—
Fe %	.002	.003	.008	.0035		.002
S %	—	—	.007	—		—
Sn %	—	—	.014	—		.043
Zn %	—	—	.002	—		.004
Insol. %	—	—	—	—		—
O %	—	—	.269	—		—
Length, inches	36	56	37.5	37	35.5	36
Width, inches	36	12	28.5	36	35.5	36
Thickness, inches	1.5	.5625	1.5	1.25	1.5	1.25
Weight, lbs.	690	112	490	550	605	525
Type of suspension	Cast lugs	Punched lugs, rings	Cast lugs	Cast lugs	Cast lugs	Cast lugs
Spacing, cen. to cen., in.	4	1.8125	4	4.375	4 — 3.5625	3.5
Life, days	26	27	30	30	30	28
Scrap, %	14.2	14	13	20	10	16.5
Anode Slimes						
per ton anodes, lbs.	2 — 3	5.8	8	2.8	12 — 16	18
Removed after ? days	26	27	30	100	15	28
Starting Sheets		none				
Length, inches	37.5		38.5	37.5	37	37
Width, inches	37.5		30.25	37.5	38	38
Thickness, inches	.025		.025	.031	.030	.025
Weight, lbs.	11.5		8.5	10	13.2	10.5
Type of suspension	1 wide loop		2 small loops	2 small loops	2 small loops	2 — 4″ loops
Cathodes						
Life, days	13	27	16 — 14	15	15	14
Weight, lbs.	290	96	215	220	270	225
Method of washing	Hot-water spray on load. mach.	Pressure spray in tanks	Dipping and spraying	Hot-water spray on wash. mach.	Spray with hot water	Hand spray
Wet flapping ?	No	No	No	Yes	No	No
Inspection — day shift ?	Yes	Yes	Yes	Yes	Yes	Yes
Inspection — P.M. shift ?	No	No	No	No	No	No

	P. D. R. C. El Paso	P. D. R. C. Laurel Hill	Raritan Copper Perth Amboy	Rhodesia C. R. N'Kana	Soc. Gen. de Hoboken	U.S. Metals Carteret
Electrolyte						
Specific gravity	1.25	1.25	1.28	1.21	1.26	1.245
Cu, g/liter	45	34.5	45	45	43	37.90
Free acid, g/liter	230	225	200	125	210	185
As, g/liter	.36	.6	12.0	.24	10 — 12	.95
Ni, g/liter	1.68	9.3	15.0	6.44	10 — 12	21.1
Fe, g/liter	.93	.35	1.5	1.54	.4 — .7	.94
Cl, g/liter	.026	.004		.025		
Sb or Bi, g/liter	.12 Sb	.50 Sb		1.68 Bi		.33 Sb
Temperature, cell inlet °C	65.6	50	60	65	60	60.6
Temperature, cell outlet °C	61.1	47.5	55.0	57.8	50	56.7
Circulation, gal. per min.	4.5	3.5	4.0	6.0	3.8	3.0
Type of pumps	Vert. & horiz. cent.	Vert. & horiz. cent.	Horiz. centrifugal	Horiz. centrifugal	Vert. centrifugal	Horiz. centrifugal
Heating equipment	Karbate tubular heat exchangers	Lead steam coils in head tank	Karbate tubular heat exchangers	Lead steam coils & Karbate heat ex.	Lead steam pipes	Karbate tubular heat exchangers
Scheme of purification B.V.* =copper sulfate Lib.**=electrolytic liberation	B.V.* production by neut. & concentrn. Fe cementation and discard	B.V.* production by neut. & concentrn. Lib.** of Cu,As,Sb Removal of Ni,Fe, etc. by concentrn.	Lib.** of Cu,As,Sb Removal of Ni,Fe, etc. by concentrn.	In process of design	Lib.** of Cu,As,Sb Removal of Ni,Fe, etc. by concentrn.	Segregation in Pyne-Green tanks Lib.** of Cu,As, Sb Removal of Ni,Fe, etc. by concentrn.
Addition Agents						
Glue, lbs./ton cath.	.09	.00009	.15 — .032	.098	.020	.065
Goulac, lbs./ton cath.			.60 — .200	*Bindarene* .127	none	Lignone .79 (50% solids)
Others, lbs./ton cath.			Casein .085		.9	
Power						
Amperes per cell	14,800	414	7,500	9,000	10,500	10,700
Cath. C.D. amps/sq. ft.	19	18.4	15.5	15.0	14.5	14.8
Cell voltage	.185	.140	.200	.230	.180	.227
Conversion equipment A.C. to D.C.	*M.G. sets*	Rotary converters	M.G. sets Diesel generators	M.G. sets	Rotary converters	M.G. sets, mech. rect., turbo-gen.
K.W. of generators	750	750 — 500	2,400	990	1,837	1,500
Amp. of generators	5,000	2,400 — 1,800	8,000	10,000	10,500	12,000
Maximum voltage of gen.	150	360 — 325	300	110	175	150
Current efficiency %	89	70	92	92	96 — 97	90
K.W. hrs./ton cath.	159	151	176	197	150	182
Lbs. cath./K.W. day	302	318	273	244	320	264
Electrolytic Cells						
Material	Concrete	Concrete	Concrete	Concrete — wood	Concrete	Concrete — wood
Lining	Antimonial lead	Asphalt	Antimonial lead	Antimonial lead	Lead	Lead
Length	13′ 2.25″	16′ 0″	10′ 0″	12′ 6″	11′ 5.875″	11′ 0″
Width	3′ 7″	5′ 4″	2′ 10″	3′ 7.5″	3′ 5.438″	3′ 6″
Depth	3′ 10″	5′ 2″	4′ 0″	3′ 11.5″	3′ 8.5″	3′ 7.75″
Anodes per cell	37	102 cells of 5 Anodes per tank	30	32	34 — 38	37
Cathodes per cell	38		31	33	35 — 39	38
System and arrangement	Whitehead	Series	Walker	Whitehead	Walker	Walker
Amps./sq. in. bus bar	400 — 600	225	600	450	520	535
Electrolyte inlet to cell	Bottom	Bottom	Bottom	Top	Bottom	Bottom

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Chapter 9

Cathode Melting and Casting of Marketed Copper Shapes

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At the present time over 80 per cent of the world production of primary copper is initially in the form of cathodes. All but a relatively small proportion of this is melted and cast into the various shapes required by wire and sheet mills for rolling and extruding. The principal forms of refined copper castings produced from cathodes are wirebars, cakes, and billets, examples of which are shown in Figure 14-1, page 339.

The three main types of copper in which the cast shapes are produced are tough-pitch, deoxidized, and oxygen-free copper.

TOUGH-PITCH COPPER

Nearly one hundred years ago Percy[1] defined tough-pitch copper as copper "which is in the highest degree malleable at all temperatures." Then, as now, tough-pitch copper was characterized by the presence of cuprous oxide, but it is only comparatively recently that the role played by this constituent has been made clear. The term tough pitch, as here used, refers to copper in the form of refinery shapes produced by melting electrolytic cathodes, and containing a controlled amount of oxygen.

Melting in Reverberatory Furnaces

Cathode melting for the production of tough-pitch copper shapes was originally carried out in small coal-fired reverberatory-type furnaces of 50 tons capacity or less. Charging was done by means of a long iron bar flattened out at one end and suspended near this end by means of a chain from an overhead crane or gantry arrangement. One or two cathodes were placed on the flattened end of this peel bar and transported into the melting chamber of the empty furnace by men on the free end. By this process charging was a lengthy and heavy operation. Withdrawing the molten charge was an even more arduous task. In its early form it consisted of continuous hand-ladling from furnace to molds by a crew who followed each other so closely in the endless circle from mold to furnace that heel burns from splashing metal was a routine hazard. The bottlenecks arising from charging and discharging techniques were gradually overcome by the development of mechanically operated ladles by Peirce[2], casting machines by Walker[3] and Clark[4], and charging equipment by Addicks[5], Prosser and Ladd[6], Clark and Antisell[7], and others. The modern reverberatory furnace used in converting copper cathodes to shapes now ranges from 250 to 400 tons capacity. Mechanized charging, the use of one or two multi-spout pouring ladles, and casting wheels of the Walker or Clark type permit the completion of the entire furnace cycle within a 24-hour period.

In a typical installation the furnace structure rests on brick or concrete piers about 4 feet in height rising from the bottom of a concrete-lined pit sunk below the charging floor level. Cast-iron plates supported by the piers provide a plane surface on which is cast a concrete slab, the upper surface of which has a concave contour. In some installations 4-inch pipes are cast in this slab and a forced circulation of air maintained for cooling. Heavy steel or cast-iron plates are placed at the sides and ends to form a rectangular enclosure in which the refractory lining is installed. The whole is held together by a system of massive structural steel columns called buckstays which are connected longitudinally and transversely by adjustable tie rods or are maintained in their supporting function by jackscrews bearing against the concrete pit wall.

That portion of the refractory lining which will be below the metal level during the greater part of the furnace cycle requires meticulous attention to design, installation, and selection of suitable refractories. The bottom is of prime importance. It is generally made of two or three courses of brick laid in the form of superimposed inverted arches matching the contour of the concrete slab. At one refinery design calls for a course of 12-inch fire-clay brick followed by a course of 9-inch silica brick with a top course of 12- or 15-inch silica brick. At another works the clay course is omitted and two 12-inch or 15-inch silica courses form the bottom. The practice of constructing a bottom from fused silica sand or a mixture of fused sand and cuprous oxide is still followed in some installations. These bottoms are said to give good service and if not misused may last as long as seven years with patching performed as required.

Side-wall construction below the metal line is in nearly all cases of burned magnesite brick backed up on the cold face with fire-clay brick.

The total thickness is typically 18 inches, including a 12-inch course of magnesite. In some instances trouble is encountered due to reaction between the silica bottom and the magnesite side wall. This has been largely eliminated by substituting magnesite brick for silica in the top course of the bottom to the extent that a magnesite shoulder is provided on which to erect the side wall. Above the metal line it is customary to use a 12-inch course of chemically bonded magnesite brick backed up with 3 inches of firebrick.

Tapholes, located in the backwall of the furnace, are slot type, built up with a refractory ramming mixture which is gradually cut away by the furnace operator during the tapping period.

Roofs are generally constructed of silica brick ranging from 12 to 20 inches in thickness in the form of a sprung arch. Recently, however, use of a suspended-type basic brick roof has been reported[8]. In the former design the arch is sprung from water-cooled skewbacks constructed of copper, steel, or a combination of these materials. Water-cooled castings are also used to protect door jambs on the charging side, the brickwork between doors, and to form the verb arch at the constricted nose-end of the furnace. The furnace stack or uptake rises from this latter location and for a large modern furnace will have a cross-sectional area of about 20 square feet. In nearly all instances a waste-heat boiler forms an integral part of the reverberatory melting installation and raises very substantially the over-all thermal efficiency[9].

The furnace may be fired with pulverized coal, fuel oil, or natural gas, the selection depending on sulfur content and general economic factors. Bardwell[10] has recorded comparative data on the use of these three fuels. He found that under similar conditions there was required per ton of copper produced 1627 Btu in the case of pulverized coal, 1441 Btu when using fuel oil, and 1670 Btu with natural gas. The corresponding stack losses expressed as a percentage of the calorific power in each fuel were 14.4, 15.1, and 21.5, respectively. Use of fuel oil or gas in preference to coal decreases the amount of slag formed and improves life of the refractories in the areas exposed to hot fly ash and combustion gases. Correct alignment of the burners, whatever the type of fuel used, is essential to minimize wear of roof and provide maximum melting rate. To ensure efficient combustion it is customary to meter the amount of fuel and air and to provide draft-recording facilities. Gas analyses are made periodically and by correlating the various data thus obtained with the melting performance, a balance may be reached between metallurgical and combustion efficiency.

Cathode melting should rationally be confined to bringing solid cathodes into the molten state under noncontaminating conditions with provision for elimination of the small amounts of sulfur and occluded gas which may be introduced with the charge. However, in reverberatory furnace practice, because of contamination from combustion gases and iron pickup from pipe and rabbles, melting of cathodes requires essentially the same procedure as for fire-refining of impure copper. It is a batch process and every effort is made to perform the complete cycle in 24 hours. One reason for this is that supervisory and operating personnel are generally assigned to specific shifts during which the same sequence in the furnace cycle is performed each day. An ideal cycle would be represented by the following tabulation:

Time Interval	*Operation*	Elapsed Time (Hrs.)
8:00 a.m. — 12:30 p.m.	Casting	4.5
12:30 p.m. — 2:30 p.m.	Charging	2.0
2:30 p.m. — 9:00 p.m.	Melting to "flat" stage	6.5
9:00 p.m. — 1:00 a.m.	Melting to "off bottom" stage	4.0
1:00 a.m. — 5:00 a.m.	Skimming and flapping	4.0
5:00 a.m. — 8:00 a.m.	Poling	3.0

In practice, such an orderly disposed timetable is not always realized and hold-over periods or a reduction in the size of charge may be required to restore the cycle to its proper schedule.

Charging is performed by means of charging cranes developed as specialized forms of equipment for steel open-hearth furnace operations. In the hands of a skilled operator up to 400 tons of copper cathodes in lifts

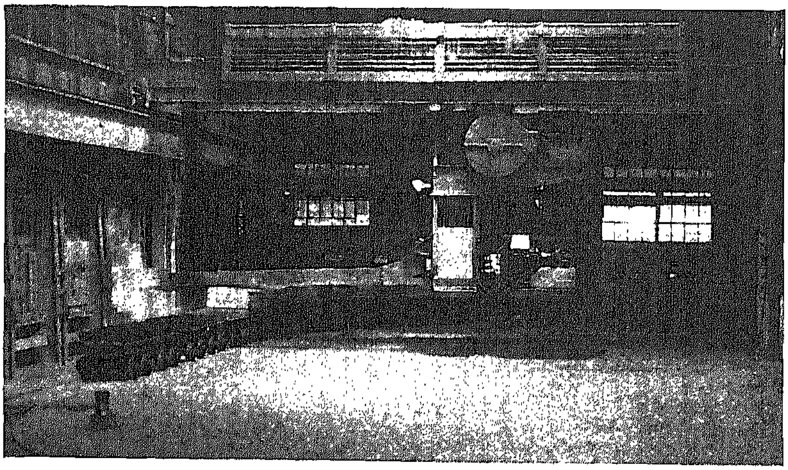

FIGURE 9-1. Mechanical charging of reverberatory furnace.

of approximately 25 pieces each is transferred within two and one-half hours from narrow-gage cars lined up in front of the furnace charging side to the furnace interior (Figure 9-1). The four hydraulically controlled charging doors provide just sufficient clearance for the charging peel with its lift of cathodes to enter and have room for lateral movement. The charge is arranged as compactly as possible, at the same time retaining sufficient free space for combustion. The furnace doors, all tightly closed, are luted with fire clay and the burners gradually turned up to the maximum heat input which can be carried without damage to refractories. After 6 to 7 hours the charge has melted down and presents a flat surface. At or just prior to this stage, an additional charge of cathodes is made, generally through the door nearest to the firing end. At this point the furnace is fully charged and melting is resumed for approximately 4 hours after the charge is completely melted and said to be "off bottom."

After a preliminary skimming, flapping is commenced. The procedure derives its name from the original practice of swinging a rabbling iron suspended by a chain so that the blade, on making contact with the bath, splashed metal through the oxidizing atmosphere of the furnace[11]. The objective, to impart an oxygen content of 0.9 per cent to the bath, is now more easily carried out by passing compressed air at 15 to 20 pounds pressure through ¾-inch iron pipes thrust beneath the surface of the molten metal. During the flapping operation a series of samples is taken to indicate the progress of oxidation. For this purpose a small ladle, known as a say-ladle, is used. It has a bowl roughly 2 inches in diameter and a depth of ¾ inch. The first button, taken with the say-ladle when the charge is off bottom will, on solidification, customarily indicate the presence of sulfur by a spew or sprouting of molten metal. As flapping is continued the convexity of the button surface changes progressively to a concave surface. A black spot appears in the center just after solidification. The spot disappears on further flapping and sample buttons are then fractured for microscopic determination of oxygen content. At 0.9 per cent oxygen (corresponding to 8.05 per cent Cu_2O) the button has a decided concavity with a bubble at the low point of the depression. On fracture, the color is dull brick-red and the structure coarsely cubical. At this point flapping is discontinued and the bath, which had previously been skimmed free of slag, is skimmed again if necessary.

The amount of slag formed will vary from 1 to 2.5 per cent of the total charge depending on the ash content of the fuel, iron pickup from flapping and skimming operations, and the degree of refractory attack. The copper content of the slag varies over a wide range and is influenced by the amount of entrained metallic copper shot. A typical analysis is as follows:

	Per Cent
Cu	26
Fe_2O_3	9.6
SiO_2	34.7
Al_2O_3	13.9
CaO	7.5
MgO	7.5

The bath is protected from reoxidation by a covering of low-sulfur pea coke, in accordance with the classical findings of Skowronski[12].

The next sequence is poling, which has as its objective reduction of the excess cuprous oxide to metallic copper. It is by this process that the refiner arrives at that residual oxygen content (as Cu_2O) which will lead to acceptable castings of tough-pitch quality. Poling is carried out by the primitive practice of inserting green hardwood poles through the skimming door of the furnace and forcing one end below the bath surface. This is generally achieved by means of an air-actuated hoist pulling upward on the free portion of the pole, causing the other end to move in the opposite direction. As fast as a pole burns away it is fed into the furnace, and when too short to be held by the hoist it is pushed in to burn as a brand on the surface. Steam and other gaseous products of combustion are evolved at a rate which causes considerable turbulence in the bath. A charge of 350 tons requires from 8 to 10 tons of poles.

The progress of reducing the oxygen content of the bath from 0.90 per cent to the tough-pitch point is determined by the appearance of block samples for set and say-ladle buttons for oxygen, which is determined by microscopic examination and reference to standard photomicrographs. Block samples, which initially are depressed and coarsely wrinkled, gradually develop a flat to slightly crowned contour with the tight, fine wrinkled surface typical of well-refined tough-pitch copper. The fractured sections from the say-ladle show a progressive change from the block or cubical structure to columnar and finally fibrous crystals. The color has changed from brick-red to rose-pink. At this stage the metal will have an oxygen content of approximately 0.020 per cent, and is ready to be cast.

Although temperature plays an important role in the melting and refining operations, use of continuous temperature recorders is not general on fuel-fired furnaces[13]. For one refinery the typical temperature range of the copper, determined by optical pyrometer, during the melting and refining operation is given as follows:

	Deg. C	Deg. F
"Off bottom"	1175	2150
Flapping, early stages	1170	2140
Flapping, later stages	1190	2175
Poling, 1 hour after coking	1160	2125
Poling, 2 hours after coking	1150	2100
Poling, at completion	1130	2070

Melting in Direct-Arc Electric Furnaces

Contamination of high-purity cathode copper, inherent in reverberatory furnace melting, has naturally turned attention to the possibilities of electric melting furnaces. The first large-scale installation of direct-arc electric furnaces for continuous melting of copper cathodes was placed in operation at Copper Cliff by the International Nickel Co. of Canada[14] in 1936. Since then a number of major refineries have installed similar equipment, some of which has been described[15, 16]. This trend has developed from consideration of economic factors, including the advantages personnel-wise of the simplified melting operation. Experience has also shown that it is possible to produce castings of more uniformly high quality over a wide range of horizontal and vertically cast shapes.

A representative installation of this type consists principally of one or more circular three-phase direct-arc melting furnaces from 15 to 18 feet in diameter, and about 10 feet in height from the low point of the dished bottom to the top of the shell. The roof is dome-shaped and readily removable. Each furnace is connected by a covered insulated launder to an enclosed pour-hearth heated by a standard low-frequency induction unit. From this vessel copper is discharged to conventional pouring ladles.

Four openings are provided in the arc melting furnace in addition to the three electrode ports: a narrow rectangular slot through which the cathodes are charged; a tapping spout diametrically opposite; a working and inspection door about 45° from the charge slot; and a circular gas take-off port in the roof. The arc furnaces are provided with an oil-hydraulic tilting mechanism, rotation taking place about an axis passing through the point in the tapping spout where a sliding connection is made with the launder. In operation the furnace is held approximately horizontal and molten copper is discharged by the displacement effect of continuously charged cathodes. The gas take-off is connected to a duct leading to wet scrubbers, cyclones, bag filters, or a combination of these units. Cathode charging is continuous by either manual or mechanical means. Views of the Copper Cliff furnaces are given in Figures 9-2 and 9-3. Functioning mainly as a means of equalizing metal flow and temperature, the pour-hearth may vary widely in design but in general the holding capacity is about 5 tons.

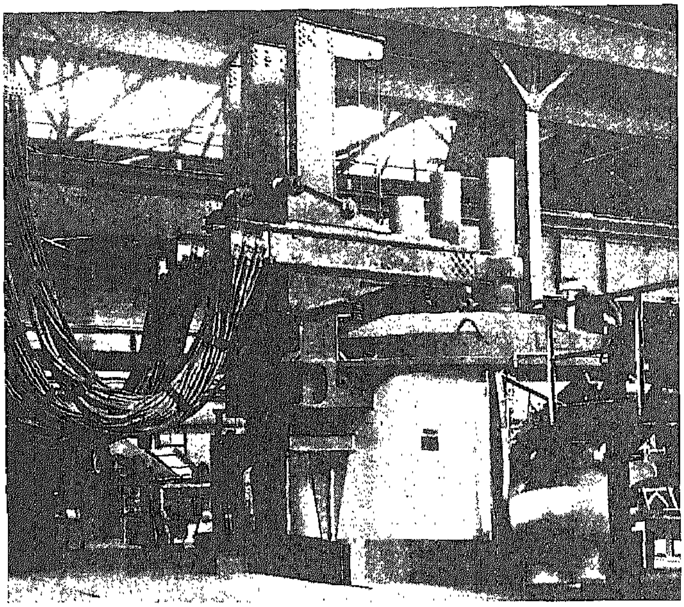

FIGURE 9-2. Arc furnace for melting copper cathodes. (*Courtesy of the International Nickel Company of Canada, Ltd.*)

With the exception of a few locations, basic refractories are used for all exposed surfaces in lining the furnace and pour-hearth. In the original installation the furnace hearths consist of fused-in magnesitic monoliths built up by fusing successive layers of periclase over preliminary brick courses. As noted by Drummond[15] the construction of this type of hearth is a lengthy operation requiring meticulous care, and this has led to the use of brick bottoms in subsequent installations, a feature which was pioneered in the plant described by the above writer.

The electrical equipment required presents no novel features other than provision for a wide range of secondary voltages from the furnace transformer. Operation is less complicated than that of ferrous electric melting practice, due largely to the steady and continuous nature of the copper-melting process. The power factor is a variable depending on the reactance of the circuit. One refinery reports better than 85 per cent power factor while in another works 70 per cent is obtained. In the former instance energy is supplied at 25 cycles per second and in the latter at 60. It is possible that this has an influence, although in electric-furnace steel practice it has been stated that no difference in power factor could be observed from a frequency difference of this magnitude[17]. Power consumption is also a variable depending on rate of melting. Between 250

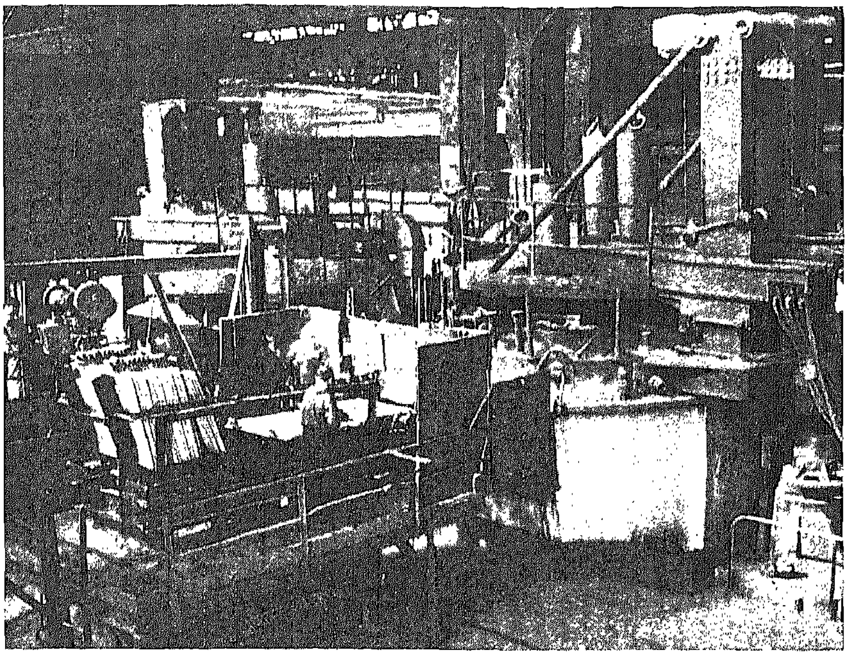

FIGURE 9-3. Charging operation, electric cathode melting furnace. (*Courtesy of the International Nickel Company of Canada, Ltd.*)

and 300 kw is required to maintain the molten bath at constant temperature with no charging and this fixed loss, when proportioned to each ton melted, will vary inversely with the charging rate. A furnace of the typical dimensions cited, melting at the rate of 15 tons per hour with metal flowing to the launder at 1200°C (2200°F) requires an average input of 225 kw-hr per ton charged. Choice of secondary voltage from the range available has an important influence on the consumption of energy, electrodes, and refractories. Thus for any given power input the operator may choose a transformer tap giving low voltage and high current or vice versa. Under the former selection the arc will be short, tending to decrease heat radiation to side walls and roof, but the high current tends to increase electrode consumption. With the same power input at higher voltage the arc will be longer, walls and roof hotter, but electrode consumption is decreased. Electrode diameter also enters into such considerations as temperature of refractories, arc characteristics, and electrode consumption. Present usage varies from 14 to 20 inches in diameter for furnace melting capacities up to 20 tons per hour.

In charging an empty furnace it is customary to transfer sufficient molten metal, if available, to form the initial bath. Alternatively light starting-sheet scrap may be melted down by means of an oil burner. In either case the objective is to secure a working pool of molten metal having sufficient volume to permit an arc being struck without damage to the refractory bottom. From this stage on, the bath is built up to the working level of from 30 to 40 tons by the normal melting action of the arc. After checking and adjusting for temperature and oxygen content, cathode charging is commenced and a flow of molten metal started by displacement. The launder, connecting the furnace and pour-hearth, will have been preheated by means of an oil burner and thereafter the heat loss occurring through this zone is small. The pour-hearth itself requires careful attention in the original start-up, and the particular technique depends on its design. One of the most important factors is proper preheating of the secondary inductor channel, and as this is generally done coincident with heating up the crucible section a special water-cooled oil-burning torch is sometimes utilized. After adequate preheating, the pour-hearth is charged with several tons of molten copper and power turned on the induction transformer, which indicates its operation by the visible circulatory motion imparted to the metal bath. The surface of the metal in the pour-hearth is partly covered with a layer of granular low-iron graphite electrode scrap.

Experience has indicated the desirability of operating arc furnaces under slightly oxidizing conditions. This is achieved by varying the amount of air drawn through the melting chamber to yield metal from the tapping spout containing about 0.010 per cent oxygen. The area of the gas take-off port in the roof may be increased or decreased by means of a sliding cover. This changes the draft, which is induced by suction fans connected to the discharge side of the dust-collecting system, and consequently the volume of air drawn through the furnace charge slot. Factors determining this volume include type of feed (clean or dirty cathodes), rate of melting, type and shape cast, and moisture content of the charge. At a melting rate of 15 tons per hour a range of from 500 to 1,500 cubic feet of air per ton of copper melted may be experienced. If an attempt is made to operate the arc furnace under conditions which tend to exclude air, the metal becomes oxygen-free, gassy, and very susceptible to contamination by metals reduced from refractory lining constituents. Should the condition continue for any extended period there is also a tendency for volatilized graphite from the arcs to condense on the surface of the bath. Gradually this layer cakes over, forming an insulating blanket which interferes with the proper functioning of the electrodes The correct draft setting may be conveniently predicted by the oxygen content of the metal, which is customarily determined microscopically on a sample slug several times per hour.

Temperature indication and control are of prime importance in electric furnace melting, where the continuous nature of the operation necessitates adherence to predetermined standards. Life of refractories, electrode consumption, and energy per unit weight of copper are all affected by temperature fluctuation, quite apart from strictly metallurgical considerations. It is usual first to make some provision for recording the temperature of arc-furnace refractories. Means by which this information is secured are radiation pyrometers sighting on silicon-carbide target blocks, or built-in base-metal couples. The circuit generally includes an alarm signal so that if an agreed-to side-wall or roof temperature is exceeded, steps may be taken before damage occurs. The next temperature control point at one refinery is in the launder, close to the furnace tapping spout, where a chromel-alumel thermocouple protected by a carbofrax tube is used. The closed end of the tube is immersed in the stream of copper flowing in the launder and gives direct information on the temperature of the metal as it leaves the furnace. At the same refinery the temperature of metal in the pour-hearth is automatically controlled by alternate connection to low and high transformer taps in response to operation of a relay by a recording controller. Here again a radiation-type pyrometer is used, sighting on the closed end of a target tube immersed in the metal bath. As a check on both thermocouples and radiation pyrometers, the temperature of the metal stream discharging from pour-hearths or pouring ladles is determined at regular intervals by means of optical pyrometers. As an example of the temperature gradient, in melting cathodes for casting into vertically cast wirebars the metal temperature leaving the arc furnace is 1215°C (2220°F), the stream from pour-hearth to pouring ladle is 1165°C (2130°F), and as the metal enters the mold it has a temperature of 1150°C (2100°F). At another installation, closed-end target tubes of nickel-chromium-iron alloy are used to take either spot or continuous readings from the pouring ladle.

The melting process as stated above is continuous, cathodes weighing from 250 to 275 pounds being charged at a typical rate of two per minute. The sill of the furnace charge slot, built of "Carbofrax," has a slope of 30°, which results in the cathode submerging beneath the bath on entry. Normally no protective covering is used on the bath, although some refractory material accumulates from time to time due to erosion and electrode ash. This is skimmed off once or twice a week as circumstances require. If melting is carried on for a lesser period than seven days a week, the furnace is carried on a holding basis over the week end and in this event skimming is conveniently carried out at such time. As charging continues, displaced metal flows down the launder into the pour-hearth, where, under a sparse covering of graphite granules, there is a theoretical retention period of about 20 minutes. This permits heat stabilization and adjustment of oxygen content if necessary. From the pour-hearth the metal falls into pouring ladles and thence either directly or through refractory funnels to the molds.

Gas-Metal Reactions in Production of Tough-Pitch Copper

Before discussion of the casting operation, it is desirable to consider at this point the more important aspects of gas-metal reactions which occur in producing molten cathode copper properly conditioned for casting in the tough-pitch state and subsequently during cooling and solidification.

The fundamental investigations of Sieverts[18], Skowronski[12], Allen and Hewitt[19], Floe and Chipman[20], Bever and Floe[21], and others have provided the foundation upon which our present understanding of gases in copper is based. A discussion by Phillips[22] on the separation of certain gases from copper and copper alloys in the molten state forms a recent and comprehensive contribution.

In a consideration of gas reactions the elements with which the producer of tough-pitch copper is mainly concerned are hydrogen, sulfur, and oxygen.

The chief source of hydrogen is from the decomposition of steam by molten copper according to the following reaction:

$$2Cu + H_2O \rightleftharpoons H_2 + Cu_2O$$

In fuel-fired furnaces steam is present as a product of combustion and in gases generated during the poling operation. In both fuel-fired and arc furnaces some steam is likely to be introduced into the system due to entrapped electrolyte in the copper cathodes. Hydrogen itself is generally believed to be absorbed or dissolved in the electrolytically deposited metal, but quantitative data do not appear to have been published on this subject. For all practical purposes steam may be said to be insoluble in liquid copper, but the products of decomposition are soluble and capable of coexistence at equilibrium in the molten bath. As solidification takes place these constituents are concentrated in the liquidus and the reaction is reversed, cuprous oxide and hydrogen combining to form steam. Depending on concentrations of the reactants and conditions under which casting is carried out, the steam so produced may either serve a useful purpose or cause unacceptable castings. The first result is obtained when the production of steam takes place at such a time and in such quantity that it offsets the shrinkage in volume which occurs during the change from liquid to solid copper. This is brought about by steam bubbles becoming entrapped in a zone just below the set surface. These bubbles should be of almost microscopic proportions and uniformly distributed. Conversely, the evolution of steam may take place earlier in the solidification process, in which case it passes from the system and the casting may exhibit a sink or pipe. If deferred until the last stages of solidification, the formation of steam may cause large isolated blowholes, rendering the casting unfit for fabricating.

Hydrogen has a high rate of diffusion and is also soluble to a relatively high degree in both liquid and solid copper. These properties, coupled with the fact that normal furnace atmospheres are not high in hydrogen content, lead to the belief that this gas does not, in itself, constitute a primary problem in producing tough-pitch copper. It is the combination of hydrogen with cuprous oxide to form steam that is important.

Sulfur dioxide is introduced into the system as a product of fuel combustion and from the decomposition of entrapped electrolyte in the cathode charge. In contact with molten copper it reacts to form cuprous oxide and cuprous sulfide, both of which are soluble in the bath. As in the case of steam and copper, the reaction is reversible and on cooling, cuprous oxide and cuprous sulfide concentrate in the liquid portion and react to form sulfur dioxide. Due to different solubilities of reactants and the products of reaction, there are differences between the reactions involved in the formation of sulfur dioxide and of steam. One important result is that under certain conditions supersaturation by the former gas can be delayed until a point barely short of complete solidification. Under these circumstances the gas is expelled with considerable pressure and gives rise to the phenomenon known as sulfur spewing.

Oxygen is dissolved by molten copper as the compound cuprous oxide, which forms a eutectic with the metal, melting at 1065°C (1949°F) and containing 0.39 per cent oxygen. As described earlier in this chapter, one of the operations involved in melting cathodes in fuel-fired furnaces is oxidation of the molten copper by means of compressed air; the reason for this procedure may now be explained. If the minor role played by the cuprous oxide in slagging off metallic impurities is neglected the following equations prevail:

$$6Cu + SO_2 \rightleftharpoons Cu_2S + 2Cu_2O$$
$$2Cu + H_2O \rightleftharpoons H_2 + Cu_2O$$

From these it will be seen that saturating the molten copper with cuprous oxide will drive the reactions from right to left, decreasing the concentration of sulfur and hydrogen to a very low figure. In the subsequent reducing or poling operation the objective is to decrease oxygen, the chief remaining impurity in the coke-protected bath, from about 0.9 per cent to about 0.020 per cent. The exact figure to which the oxygen content may be lowered without disturbing the desired equilibrium between this element, sulfur, and hydrogen will vary for individual installations and even between charges. In general, the oxygen is adjusted by poling the charge within the furnace until a sample block shows a flat or very slightly crowned set surface.

Reference should be made to the condition known as "overpoling." Skowronski has defined overpoled copper as copper which has been excessively reduced during the poling period of the refining process and which, due to the resulting porosity on casting, is unfit for commercial purposes. In general, overpoled copper exhibits one or more of the following visible defects: it may spew, *i.e.*, eject wormlike exudations of metal at the moment of solidification; it may develop a broken puffed ridge along the center of the set surface; the set surface may be excessively convex or crowned; there may be blisters on the set surface. The internal structure of overpoled copper generally reveals wormlike gas cavities and blowholes of various types.

From his investigations Skowronski concluded that sulfur is a direct agent in overpoling and that the amount of oxygen which may be present in the tough-pitch state is controlled by the sulfur content and the presence of other reducing gases. In this respect, it is believed that the effects of sulfur and hydrogen in oxygen-bearing copper are similar and probably additive.

Consideration of gas-metal reactions points up some important distinctions between fuel-fired and electric arc furnaces for the melting operation. Once a fuel-fired furnace charge is ready for casting it must be taken out as quickly as possible so that the inevitable reabsorption of hydrogen and sulfur from the furnace atmosphere will not be excessive. If this is not done the established equilibrium conditions may be disturbed sufficiently to cause the charge to "go high" in similar fashion to the results obtained when copper is overpoled. This places certain restrictions on the operator in respect to his freedom to vary such factors as oxygen content, metal temperature, and pouring speed. Assuming a clean charge, this situation does not exist in electric-arc melting furnaces due to the absence of contaminating products of combustion.

Casting Tough-Pitch Copper

Tough-pitch copper castings must meet certain requirements in respect to composition, surface quality, and internal soundness to comply with established commercial standards. In many instances such standards represent a minimum, and production is under substantially stricter specifications imposed by internal quality control or arrangement with customers. The set surface should be flat to slightly crowned, finely wrinkled, and free from ridges or edgewise depressions. Other surfaces should be free from laps, cold sets, inclusions, and exudations. Internally there should be no blowholes or cracks. Consistent production of high-quality castings requires that the molten metal be properly conditioned with respect to gas content and amount of gas-forming elements. The means for pouring the molten metal into the mold must permit a quiescent transfer so as to avoid the surface defects referred to above. Temperature range, pouring speed, and mold design will determine the rate of solidification, which in turn will influence the internal structure. These conditions will be discussed in more detail below.

Refinery shapes are of two classes: regular shapes consisting mainly of horizontally cast wirebars, ingot bars, and ingots; and special shapes which include vertically cast wirebars, cakes, and billets. In either case large-scale production is facilitated by means of specialized equipment integrated with the melting unit. The conventional form of casting machine is a turntable or wheel from 25 to 42 feet in diameter, horizontally disposed in front of the melting furnace. Auxiliary equipment includes pouring ladles, cooling boshes, and conveyor systems. If the wheel is of the Walker type, regular shape molds are arranged tangentially about the circumference. On the Clark wheel the molds are in a radial position, as shown in Figure 9-4. With the increasing demand for special shapes there is a trend toward casting wheels which permit production of either the horizontally or vertically cast product. The original fluid-drive cable-and-winch arrangement for rotating the wheel smoothly is now frequently replaced by direct gear-and-pinion drive with electronically controlled acceleration and deceleration.

In plants where production of special shapes is not large the practice of side-casting is employed. This involves the use of ladles or portable holding furnaces 5 to 10 tons in capacity. Copper is tapped to these from an auxiliary taphole in the main melting unit from time to time and, after adjustment for temperature and oxygen content, the metal is cast into molds located on a rack or small wheel.

Molds for horizontal casting are tray-like, the major axis lying in a horizontal plane. They are made by lowering water-cooled cores, conforming to the desired mold cavity, into molten copper contained within a mother mold. As soon as the copper sets, the cores are withdrawn and the mold casting removed. Such molds are of massive section and, having a life of only a few days, require frequent replacement. In service, they are maintained within the desired temperature range by water sprays playing on the bottom. Shapes cast in this type of mold are now largely restricted to wirebars, ingot bars, and ingots, but some production of flat cakes continues.

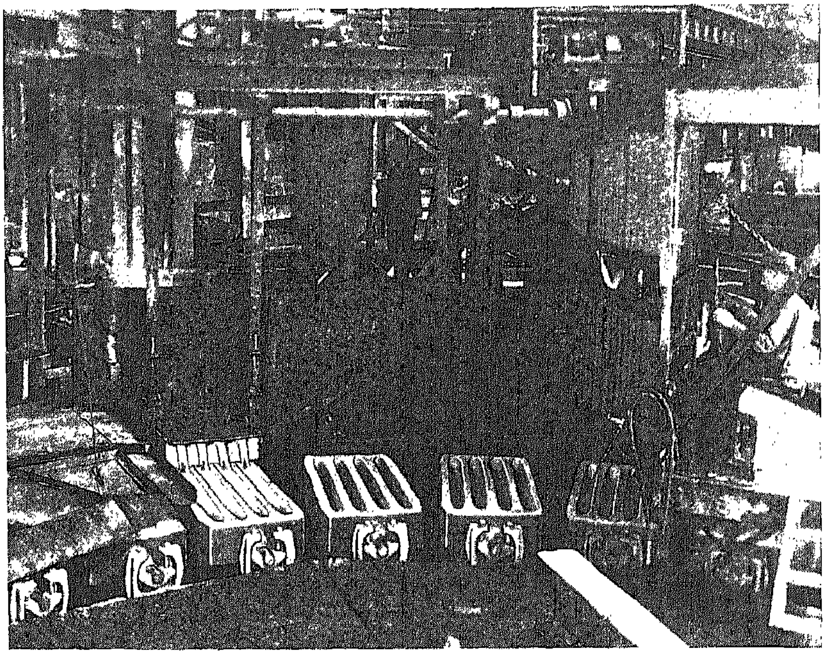

FIGURE 9-4. Pouring horizontal wirebars on Clark wheel.

Vertically cast shapes are produced in molds having the mold pocket in a vertical plane so that the set surface of the shape is of minimum area. Molds of this type are generally constructed of copper with machined pockets and heavy side walls which are drilled to provide a system of internal channels for the circulation of cooling water. A variation, used chiefly in producing billets and wirebars, consists of square or circular copper tubes encased in steel jackets with provision for circulation of cooling water between jacket and tube. In either case the bottom is formed by a heavy copper slab mounted in a hinged iron frame. Assembly of internally cooled molds on a casting wheel requires a water distributing system, usually composed of upper and lower circular headers connected by spoke-like branches to a central rotary hub. Feed and return mains lead to separate annular channels in the hub and serve the two headers. Each mold is provided with inlet and outlet connections, water entering at the bottom and leaving at the top. The mold assembly customarily forms a link in a closed system comprising supply tank, circulating pump, and heat exchanger. An arrangement of molds for large-scale production of vertically cast wirebars at Copper Cliff is shown in Figure 9-5.

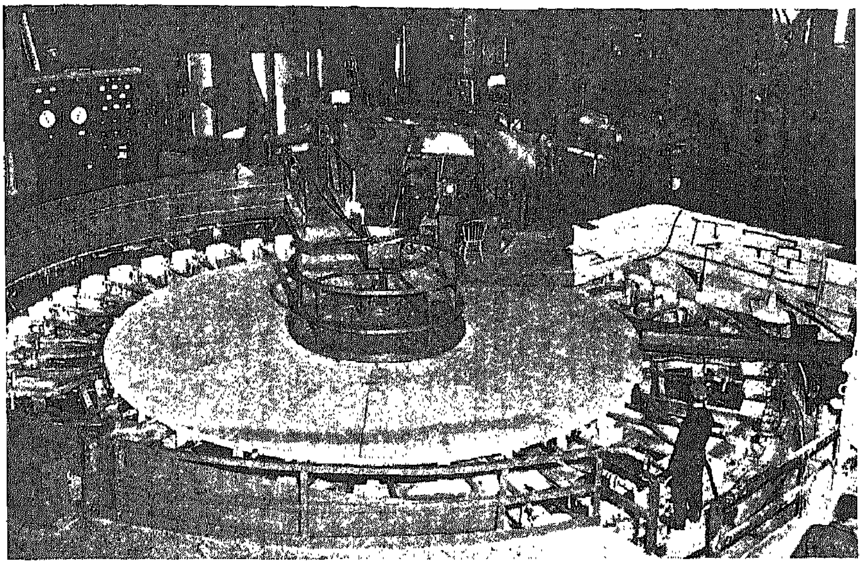

FIGURE 9-5. Pouring vertically cast wirebars from electric furnace. (*Courtesy of the International Nickel Company of Canada, Ltd.*)

Whatever class of shape is under production, a mold dressing must be applied before each filling. The primary functions of the mold dressing are to prevent contact between the molten copper and the mold surface, which would cause sticking, and to provide an insulating film which prevents laps due to copper solidifying before conforming to the mold surface. This insulating effect also minimizes the occurrence of cold sets caused by surface inclusion of small copper particles ejected from the pouring stream and solidified against the wall of the mold. The material used universally in casting tough-pitch shapes is an aqueous suspension of bone ash. Over 75 per cent tricalcium phosphate, bone ash adheres well to the mold surface, is not wetted by copper, imparts no impurities to the metal, and is free of volatile constituents. Density of the suspension used will vary over wide limits according to type of casting and the characteristics of the bone ash. It is applied by means of spray guns to open-face molds, and may be simply flowed on in deep vertical-type molds. In areas where there is excessive wash, such as the bottom of vertical molds, a heavier coating is applied; this procedure is also used to retard the formation of "sweat" or exudation of metal high in cuprous oxide from the casting. Water used for suspending bone ash must be free from organic matter and low in dissolved or suspended mineral substances. In some instances, benefits have been reported by adjusting the hydrogen-ion concentration of the suspension to a constant value.

Mold temperature is an important consideration in establishing proper casting conditions. If permitted to exceed certain limits the life of the mold will be reduced and the surface quality of the casting impaired. If the temperature is too low the mold dressing will be streaky and may retain water, leading to porosity or to an explosive reaction with the molten metal. In the production of horizontally cast shapes, it is customary to maintain the molds within a predetermined range of temperature by adjusting external water sprays. Temperature readings are made periodically by inserting a thermometer into a well drilled in the mold wall or by means of a surface-contact type pyrometer. Internally water-cooled molds used for vertical casting are usually automatically maintained between 88 and 99°C (190° and 210°F) by thermostatic control of the heat-exchanger operation.

Pouring practice varies substantially depending on whether horizontal or vertical molds are used, and also according to the shape of the casting. Common considerations, however, are that the metal stream from ladle to mold should be smooth and unbroken; it should not impinge on the mold wall; and there should be a minimum of splash and turbulence. The free-falling stream should be kept as short as possible to prevent a ragged flow and minimize pickup of oxygen. This is difficult in pouring deep vertically cast shapes. The rate of pouring should be considered in relation to the temperature of the metal, shape of casting, and type of mold. As a broad generalization, and in respect to vertically cast shapes only, the combination of relatively high pouring temperature and low pouring speed is believed to give the best compromise between the conflicting requirements of freedom from shrinkage defects and freedom from surface defects and blowholes due to air entrapped by the metal stream[23]. It is apparent that careful attention must be paid to the design of the pouring ladle, its tilting mechanism, shape of lips, holding capacity, and skim bridge. The same care is necessary in respect to funnels or hand-ladles used in vertical casting. When cakes are cast according to the latter procedure an additional aid is sometimes invoked to reduce surface defects due to splash in the initial stage of pouring. As the metal stream breaks from the tilting ladle it is received in a small metal bowl shaped like a pelican's pouch and attached to a long handle. Continuously receiving the metal stream, an operator quickly lowers his ladle to the bottom of the mold and there discharges the molten metal to provide a splash pad in which the force of the now freely falling stream of copper is absorbed.

The temperature of the metal is also varied in accordance with the type of shape. For example, in producing horizontally cast wirebars on a Clark wheel, it is the practice to maintain as low a metal temperature as possible, consistent with freedom from skulling in the pouring ladle, which would distort the contour of the stream. In one refinery the channels in the pouring ladle are electrically heated to permit a pouring temperature of about 1100°C (2000°F) without freezing of metal in the ladle[24]. Use of the Walker wheel permits more latitude in choice of pouring temperatures due to the mold being in motion during the pouring operation.

The production of tough-pitch shapes with acceptable set surface is achieved by varying the concentration of gas-forming reactants in the metal as casting proceeds, by adjustments to metal temperature, and by increasing or decreasing the speed of pouring. Gas formation to promote the desired level or crowned set surface is accelerated or suppressed by lowering or increasing the cuprous oxide content of the metal. To lower the oxide content, the charcoal covering the metal in the pouring ladle is stirred and worked into intimate contact with the metal. The charcoal reacts to reduce cuprous oxide to metal and at the same time, as a secondary effect, gives off absorbed gases which are dissolved in the molten copper. If the reverse effect is desired no working of the charcoal is done. Raising the metal temperature tends to increase the solubility of gases which are involved in establishing the set and, in general, a higher metal temperature in the furnace will result in castings with higher set. Variation in pouring speed will also cause variation in set, the relationship depending on type of shape being cast.

On removal from the cooling bosh by conveyors the cast shapes move into an inspection conveyor where each casting is carefully examined for surface defects, dimensional variations, and set. Sub-standard production is either summarily rejected, in which case the casting will be remelted, or set aside for further inspection. Superficial blemishes are generally removed by chipping or grinding, but the degree of overhauling is small. Special shapes such as cakes, billets, and vertically cast wirebars are frequently cut to specified lengths. In respect to the latter shape, a special machining operation has been developed[25] by which a streamlined nose or point is formed on each end of the bar to facilitate entry into the various passes of the breakdown mill. A view of this type of bar is shown in Figure 9-6.

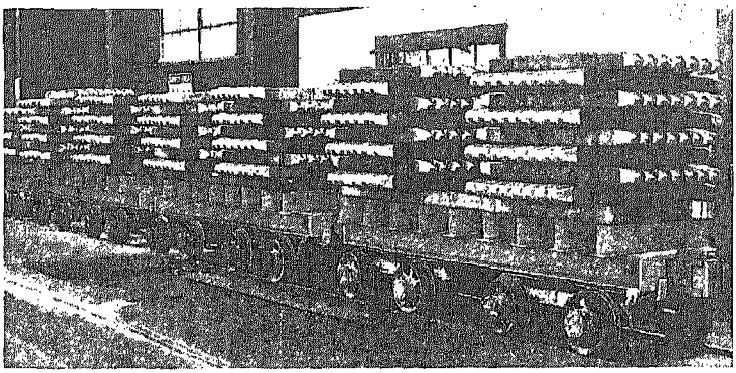

FIGURE 9-6. Vertically cast pointed wirebars. (*Courtesy of the International Nickel Company of Canada, Ltd.*)

DEOXIDIZED COPPER

An appreciable quantity of copper in a deoxidized state is required by industry, chiefly in the form of cakes and billets. This is copper which has been rendered essentially free from cuprous oxide through the use of metallic or metalloidal deoxidizers. In spite of various advantages claimed for lithium[26] and other deoxidants, the rapid and efficient action of phosphorus has led to its almost universal use in producing deoxidized copper. Phosphorus reacts with the cuprous oxide in oxygen-containing copper to form an insoluble and volatile oxide believed to have the formula P_2O_5[27]. Copper which has been deoxidized with phosphorus and retains residual quantities ranging from 0.015 to 0.040 per cent is called high-residual phosphorus copper. The excess phosphorus goes into solid solution and causes a substantial decrease in electrical conductivity, increase in softening temperature, and corresponding increase in hot strength. When the residual phosphorus is in a range of approximately 0.004 to 0.010 per cent, the product is called low-residual phosphorus copper and in this case the conductivity is less severely affected[28].

The production of phosphorized copper proceeds along the same lines described for the tough-pitch variety up to the point where the molten metal is being prepared for casting. At this point the copper is deoxidized by addition of an alloy of phosphorus and copper containing about 15 per cent phosphorus. The mechanics of addition varies widely. If side casting is being done the addition of the master alloy may be made to the portable holding furnace by plunging a perforated graphite vessel containing the master alloy below the surface of the bath. Another procedure is to add the calculated quantity of deoxidant to the ladle just before pouring into the mold. In continuous electric melting practice the master alloy is added to the launder in powdered form by means of a continuous feeding device.

Removal of cuprous oxide from the system eliminates the formation of steam and sulfur dioxide, characteristic of production of tough-pitch copper. There is no level-set effect, the metal exhibiting normal shrinkage characteristics and, assuming no undue solution or entrainment of gases, the castings develop a deep pipe which may be partially offset by feeding.

The production of phosphorized copper castings requires a mold dressing which will produce a smoky reducing atmosphere during pouring. Although the makeup and proportions of such a dressing will vary widely between different refineries, in general the constituents consist of a carbonaceous material such as bone black, lampblack, or graphite suspended in a heavy mineral oil. Sometimes bone ash is added to the mixture as a filler. Preferably, the solid constituents, together with the selected volume of oil, are placed in a pebble mill or similar equipment and mixed for several hours until a smooth, uniform suspension is secured. To minimize changes in viscosity the dressing should be stored in containers maintained at constant temperature. The dressing is applied to the molds by means of swabs made from felt segments, lambskin, or other materials which will lead to a smooth, uniform application. After each filling it is customary to clean the charred residue from the molds by means of mechanically actuated wire brushes. Freedom from unsoundness due to gaseous products of reaction results in castings of higher density than are secured when casting tough-pitch copper. Changes in surface tension of the metal, presence of a certain amount of copper phosphate slag, and unburned carbonaceous residue from the mold dressing require special consideration in attaining an acceptable surface. In respect to the last-mentioned item a procedure has been developed[29] which greatly reduces the chances for formation of surface defects from this source. Immediately after the formation of a pool of copper on the bottom of the mold, a very small stream of water is introduced coincident with the molten copper. This results in the formation of a large number of water globules which float on a layer of steam between themselves and the surface of the molten metal rising in the mold. The granular carbonaceous particles are collected by the water and repelled from the oily surface of the mold, thus preventing their inclusion in the surface of the casting.

OXYGEN-FREE COPPER

A special process for producing cast copper shapes, free from cuprous oxide, without the use of metallic or metalloidal deoxidizers, was brought to a successful stage of development about 1930. Known as the "Oxygen Free High Conductivity Process," this method of production is in operation at the United States Metals Refining Co., Carteret, N. J., and at the Outokumpu Mining Co. at Pori, Finland[30].

Prime-quality copper cathodes are melted in specially designed low-frequency induction furnaces under non-oxidizing conditions brought about by use of a graphite granule bath covering, plus a flow of dry reducing gas through the melting vessel. If desired, means are provided for preheating the cathodes, which drives off the sulfur in occluded electrolyte. The flowing protective atmosphere, which is low in hydrogen, helps to reduce the concentration of this latter element if present in the bath.

From the melting furnace the metal is conveyed to a pour-hearth which is also heated by a low-frequency induction unit. The connecting launder is totally enclosed and heat losses are offset by the use of Globar resistors. A protective gas atmosphere prevents contact of the molten copper with air at all locations, and in order to continue this protection to the point where the copper is cast and fully solidified, a special hood connects the pour-hearth and molds. This hood is a structural enclosure containing multi-outlet pouring funnels, Globar resistors, and a protective gas atmosphere. It is articulated to accommodate the movement of the pour-hearth when tilting and also makes a seal with the top of each mold as the latter is brought into position by the casting wheel.

Before pouring, the bottom door of each mold is partially opened and the protective gas atmosphere under positive pressure within the hood sweeps all air from the mold. The bottom doors are then closed, the hood sealed to the mold top, and pouring is commenced. The rate of pouring is slow so that solidification is essentially from the bottom up and sufficiently advanced at all times to prevent formation of a deep pool of molten metal which might entrap gas and cause porosity.

The molds are vertical-type, consisting of a plurality of suitably shaped steel tubes enclosed in a steel water jacket. Mold dressing is generally a suspended mixture of bone ash and bone black in water having a specific gravity between 15 and 20° Bé.

Copper shapes produced by this process solidify with the deep shrinkage pipe characteristic of copper which is free from oxygen. No cuprous oxide can be detected by microscopic examination at a magnification of 75 diameters. A general view of the Carteret installation is shown in Figure 9-7.

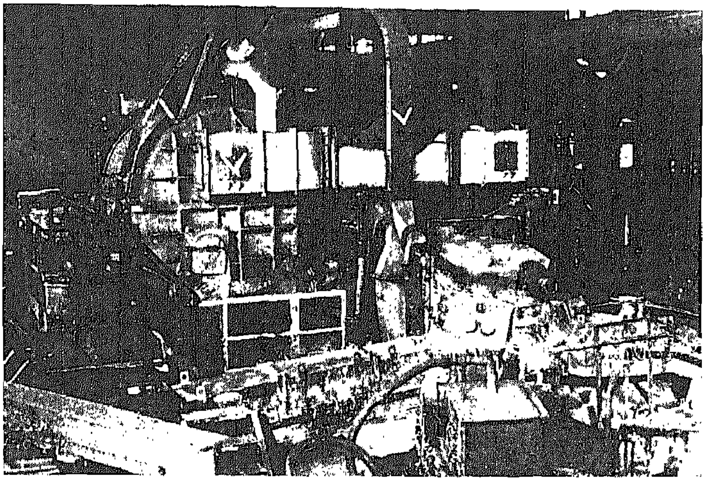

FIGURE 9-7. Installation for producing oxygen-free copper. (*Courtesy of the American Metal Company.*)

An entirely different approach to the production of oxygen-free copper shapes was conceived by Stout in 1925[31] and a process based on his findings has been put in operation by the Phelps Dodge Copper Products Corporation. In this process[32], regular copper anodes which are free from siliceous mold wash material are electrolyzed to produce a cathode deposit on a copper blank from which it can be easily stripped. The electrolyte is treated with addition agents resulting in an extremely friable deposit capable of being easily broken into small fragments. These particles are washed and briquetted under pressure of 20,000 psi to form a porous mass. The briquettes are charged to a controlled-atmosphere heating furnace and heated to about 900°C (1650°F) in a deoxidizing gas, upon which any traces of oxygen are removed and a substantial reduction in arsenic, antimony, and sulfur content takes place. The sintered briquettes then pass into an extrusion press where, under pressures up to 76,400 psi, coalescence takes place, resulting in complete crystal growth between all particles at temperatures well below the melting point. The product is extruded in the form of bars, rod, strip and other commercial shapes[33].

CONTINUOUS CASTING

Continuous casting is a process by which metal in the molten state, fed into one end of a mold or forming enclosure, is continuously withdrawn in the solid state from the other end at a speed coordinated with the rate of solidification. Although the principle of continuous casting is not new[34], it is only within recent years that this procedure has been successfully utilized to cast refined copper shapes on a commercial scale. At the present time production is confined to phosphorized and oxygen-free copper, but casting of tough-pitch metal is also under investigation.

Three continuous casting processes for the production of copper shapes are in operation in the United States. The Asarco process was installed at the Perth Amboy plant of the American Smelting & Refining Co. in 1937[35]. Cathodes are melted in Detroit electric arc furnaces and the metal poured into an electrically heated casting furnace. The latter is essentially a graphite-lined chamber with a bottom outlet in the form of a water-cooled graphite die. Solidification occurs rapidly as the casting is withdrawn through the die by suitable pinch rolls. Castings are cut to length by a moving cut-off saw and, in the case of piercing billets, are scalped to remove any surface imperfections. The Asarco process is characterized by the absence of a free-falling stream into the forming die, which is fed by simple gravity flow from the melting furnace. This eliminates the entrapping of gas or air by mechanical means and simplifies the problem of maintaining a constant rate of metal flow to the mold or die.

At the United States Metals Refining Co. plant at Carteret, N. J., two processes are used in the continuous casting of oxygen-free copper. The Welblund-Benard or Inco machine is used for casting bars and small billets[36]. Molten metal from the Oxygen Free High Conductivity cathode melting equipment is laundered to a hooded enclosure which makes a gas-tight seal with a vertically split, water-cooled copper mold. The inner mold surface is chromium-plated and the two mating sections define an open-ended chamber. Horizontal movement is imparted to each mold section at a frequency of about 1,200 cycles per minute. The amplitude ranges from 0.005 to 0.010 inch. The bottom of the mold is initially closed with a starting plug or dummy bar and, as molten metal is introduced at the top, the starting plug or dummy bar is continuously withdrawn by the action of pinch rolls. The effect of the mold vibration is to produce rapidly recurring pressure on the solidifying metal and at the same time relief is afforded against the tendency of the metal to rupture or tear at the surface as withdrawn. As the casting leaves the mold it passes through a high-velocity spraying device where cooling is completed. As a further means for reducing friction between the casting and the mold wall a hydrocarbon gas is introduced into the hood enclosing the top of the mold[37]. On contact with the molten metal the hydrocarbon gas is dissociated into hydrogen and soot-like particles of carbon. The latter deposit on the metal meniscus and are carried to the mold wall to form a lubricant between the mold and the copper casting. The concentration of hydrogen is controlled by circulation of an inert gas through the hood. The surface of the castings produced is good, but rate of production is restricted to from 1.5 to 2 tons per hour.

The second installation at Carteret consists of a Junghans-Rossi machine[38], which produces circular billets up to 8 inches in diameter and slabs or cakes in two sizes, 4 by 13 inches and 3½ by 26 inches. This unit also receives its supply of molten copper from the oxygen-free process cathode melting furnace. A characteristic feature of the Junghans-Rossi machine is the one-piece copper mold which reciprocates in a vertical direction. During its downward movement the mold travels at exactly the same rate as the casting, which is withdrawn by a conventional pinch-roll arrangement. At the end of the down stroke, which is about 1½ inches in length, a cam mechanism comes into action and, at a speed about three times that of the downward traverse, returns the mold to its upper position. During that part of the cycle in which the mold moves downward there is no relative motion between mold and casting. At this time a shell of solidified metal is formed against the mold surface, from which it is subsequently stripped by the inertia of the casting acting against the quick upward thrust of the mold. The movement of the mold results in a constantly changing section of the mold wall being brought into contact with the molten metal, which increases the rate of heat transfer. The low frequency of relative movement between mold and metal tends to minimize rupture of the skin, and additional relief is secured by the use of lubricants. Casting rates substantially higher than those reported for the Asarco and Inco processes are obtained.

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Chapter 10

Induction Melting of Copper and Copper Alloys

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Historical Outline

When the core-type induction furnaces for melting metals were conceived about sixty years ago, the attention of the inventors was directed chiefly to the production of steel. At that time, arc furnaces had not yet been fully investigated, and the induction principle seemed to provide an answer to the melting problems of the steel industry. A number of induction furnaces, some of them of large capacity, were made for the melting of steel, and the names of Colby in the United States, Roechling and Rodenhauser in Germany, and Kjellin in Sweden are closely connected with this development.

The chief application for the core-type induction furnaces, however, has become the field of nonferrous metals and alloys. J. R. Wyatt built his first commercial induction furnaces for the melting of brass during the years 1915-1917[1], some of which were installed at the Bridgeport Brass Co., Bridgeport, Connecticut. Ajax-Wyatt furnaces are now universally accepted as the standard melting equipment in brass mills.

The development of melting furnaces of larger production capacity has been greatly stimulated by the advent of continuous casting machines in recent years. The 2,100-kw Summey furnace[2] for melting of copper cathodes at the U. S. Metals Refining Co., Carteret, N. J., was started in 1929, and connected to a continuous casting machine in 1948; it still represents the largest induction furnace ever built for melting copper. In 1949, the Scovill Manufacturing Co. in Waterbury, Conn.[3], installed three 1,000-kw Ajax-Scomet furnaces to supply a continuous casting machine with molten brass. These furnaces constitute milestones in the history of induction melting, a development which has by no means come to its conclusion.

Principles of the Induction Furnace

The core-type induction furnace operates on the principle of a short-circuited transformer[4]. Figure 10-1 shows the fundamental parts of the electric circuit. Alternating current of power-line frequency is applied to the primary coil (A), made of high-conductivity material. The coil surrounds a laminated core (B), made of low-loss high-saturation steel and provided with forced air cooling. The ring (C) surrounding the primary coil represents the molten metal, which is contained in a receptacle of refractory non-conductive material, not shown in the diagram.

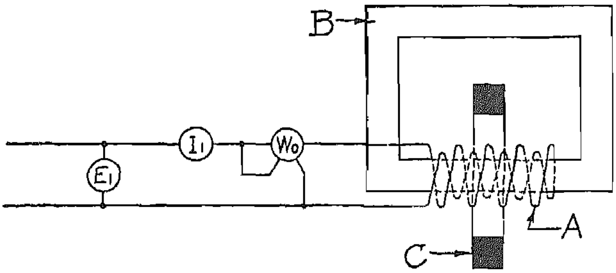

FIGURE 10-1. Basic electric circuit of an induction furnace.

That part of the furnace which, in a steel case, contains the primary coil, the laminated steel core, the secondary channels, and the cooling fans or blowers will be called briefly the "inductor unit." It is attached to a hearth preferably of cylindrical shape. New metal is charged into the hearth, the melting of which is effected by contact with hotter metal emerging from the inductor unit.

If an alternating electromotive force (E_1) is applied to the primary coil having n turns, a primary current (I_1) will flow. At the same time, a secondary current of the magnitude $I_1.n$ will flow through the molten metal loop (C) in the opposite direction. The secondary current is usually very large and creates heat in the secondary circuit, having a resistance R_2, according to Joule's law:

$$W_0 = I_1^2 \, . \, n^2 \, . \, R_2$$

The efficiency η of the furnace is given by the equation

$$\eta = \frac{W_0 - W_i}{W_0},$$

where W_o is the operating power and W_i the idling power, *i.e.*, the energy required to hold the molten metal at a constant working temperature. W_i is composed of the very small copper and iron losses in the transformer and of heat losses through the furnace walls and the charging opening of the furnace. These heat losses are determined by the dimensions of the walls and heat conductivity of the refractory and insulating materials used for their construction.

Measurements made on the primary side of the furnace circuit show that the current is out of phase with the voltage, the lag being determined by the phase angle ϕ. Voltage, current, power, and phase angle are linked by the following equation:

$$W_0 = E_1 \,.\, I_1 \,.\, \cos \phi,$$

where W_0 is the power in watts, E_1 the primary voltage in volts, I_1 the primary current in amperes, ϕ the phase angle, and $\cos \phi$ the power factor.

If the voltage is varied and measurements are made without otherwise changing the circuit, it is found that the power varies with the square of the voltage, that the current varies proportionately to the voltage, and that the power factor does not change. The induction furnace can, therefore, be considered as an apparatus with constant impedance.

In electric circuits of this type, the reactance (Y) can be considered constant as long as the shape of the secondary circuit is not changed. If metals with different resistivities are charged, the resistance will vary.

Figure 10-2 shows the performance chart of a 60-kw furnace. Power,

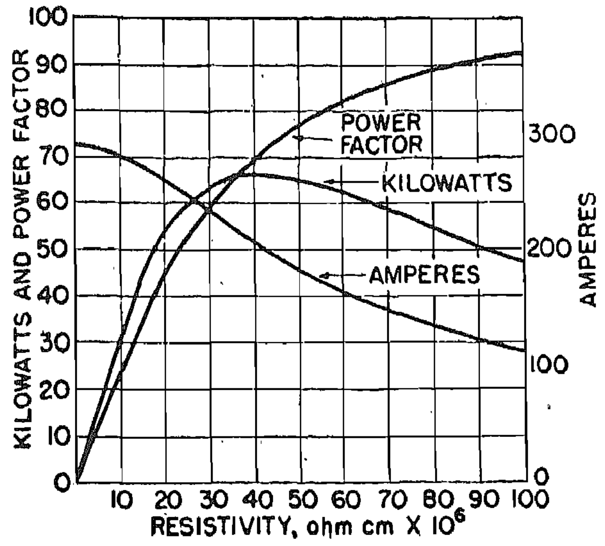

FIGURE 10-2. Performance chart of a 60-kw induction furnace.

current, and power factor are plotted in this graph for changing specific resistances of the metal charged. The chart shows that the maximum power is obtained for a power factor of 0.707, which is $\frac{1}{2}\sqrt{2}$. The maximum power is obtained from a furnace of given design when the reactance is equal to the resistance, or when the phase angle ϕ is equal to 45°, or when the power factor cos ϕ is equal to 0.707. The reactance of the circuit is given by the geometrical shape of the secondary, which determines its coefficient of self-inductance (L) in henrys and the frequency (f), according to the equation

$$Y = 2\pi \cdot f \cdot L.$$

The heat is generated exclusively in the inductor unit, which usually represents only a small fraction of the total holding capacity of the furnace, somewhere between 10 and 20 per cent. A large amount of energy is concentrated here in a small space, and it is important to make proper arrangements for a quick and efficient heat transfer from the inductor unit to the bulk of new unmolten metal contained in the hearth. Due to electromagnetic forces, chiefly the pinch effect, such a movement of the hot metal is created. In a properly designed furnace, the agitation thus achieved is violent and heat is quickly dissipated, as can readily be demonstrated by recording the temperatures at the hearth and at the bottom of the melting channels. The temperature difference between these two points is surprisingly small; it varies from 20 to 100°F, depending upon the size of the furnace and the shape of the melting channels.

Electrical and Metallurgical Characteristics

Furnaces in sizes up to 300 kw are usually constructed as single-phase furnaces with only one inductor unit. The unbalance of power in three-phase systems, an objectionable feature, is mitigated by the installation of a large number of single-phase units which can easily be distributed among the three phases of the power line. Larger furnaces are provided with two or more inductor units and connected with full balance of load in a three-phase supply. If the number of inductor units is two or a multiple of two, the inductors are arranged in a Scott connection to the three-phase supply. If this number is three or a multiple of three, each inductor is attached to one phase of the three-phase line, thus giving a complete balance of load. Up to the present time there is no induction unit available for fully balanced three-phase connection.

Induction furnaces constitute an inductive load, the lagging power factor ranging from 0.40 to 0.70, depending upon the size and construction of the secondary loop. In all cases it is economical and advantageous to connect electrostatic capacitors parallel to the primary coil to improve the power factor, thus reducing the initial cost of the electric control equipment and the power rate.

In recent years these furnaces have been provided with automatic temperature controllers. In the melting of brass, the automatic control was not considered important for a long time because the "kicking" of the ammeter, caused by overheating in the melting channels, was a signal that the proper temperature had been reached. In furnaces with higher power input, this simple method of temperature regulation is no longer sufficient. The use of thermocouples and potentiometer-type automatic controllers for maintaining uniform temperature has shown a decided advantage by further reducing metal losses. In copper melting the automatic control is indispensable.

All the refractory parts of the furnace, including the melting channels, constitute a monolithic structure prepared by ramming refractory cement with air hammers around wooden or metallic forms accurately located within the steel case. Sufficient water, and in some cases sodium silicate, is added to impart the proper binding conditions, care being taken to avoid an excess of moisture. Ramming is an operation which requires meticulous attention. The lining is gradually developed by building up successive layers of refractory mixture. On completion, the forms are either withdrawn or burned out, depending upon their construction, leaving the channel open for the secondary loop and the opening for the primary coil. The hearth or crucible part of the furnace is rammed in the same manner around a collapsible metallic form. After completion of ramming, the lining is subjected to a drying and then to a firing procedure before the furnace is started.

The most practical way to start induction furnaces is to prime them with molten metal of the proper composition after firing. The same procedure applies when alloys are to be changed, in which case it is necessary to empty the furnace and fill it with the new alloy.

Inherent with the induction furnace is the necessity of keeping a heel of molten metal at all times, whether the furnace is in production or not. Thus, the metal must be prevented from freezing during night hours, Sundays, and holidays because the shrinking of the metal contained in the secondary loops would crack the refractory lining. Holding power is of the order of 15 to 25 per cent of the rated power, depending upon the size of the furnace. In some brass mills, a technique has been found of freezing and unfreezing the furnaces at will without damaging the lining, a procedure practiced during long shutdown periods.

The induction furnace is a "cold top" furnace, a feature beneficial in nonferrous melting but detrimental for steel, which requires high temperatures at the surface for slag reactions. This method of melting has, therefore, been successful not only for copper and copper alloys referred to in this paper, but also for aluminum, zinc, lead, and their alloys.

Brass Melting

In melting brass, the most important consideration is that of reducing the zinc losses, as was eloquently explained by Gillett and Mack[5], who, in 1922, made a thorough survey of the savings to be expected from the use of electric induction furnaces in the brass industry. Their predictions have been fully confirmed and surpassed, and today copper-zinc alloys are melted almost without exception in induction furnaces all over the world. Fuel-fired reverberatory furnaces are ruled out for melting brass due to their inherent high melting losses. The only fuel-fired melting devices used before the advent of electric furnaces were crucible furnaces of small capacity. The introduction of electric melting eliminated the costly clay-graphite crucibles. Furthermore, the induction principle allows the concentration of enormous power in a small volume. Hence, while the crucible furnaces were of limited production capacity, induction furnaces have continuously increased in size and power input, so that man-hours required for melting a given amount of brass have been reduced by the electric furnace to a fraction of what they were in the times of the crucible furnace. Roughly, it can be stated that while one man was able to melt about 500 pounds of metal per hour in the old-time crucible furnace, a man can produce about 10,000 pounds of metal in the modern high-power induction furnace.

Besides these economies, which are readily recognizable in dollars and cents, there are other advantages less easily calculated but not less real. The cooler and cleaner working conditions, the elimination of much hard

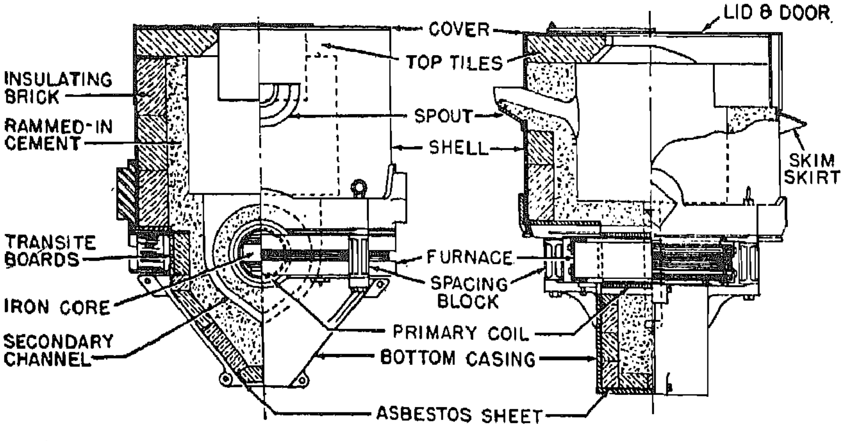

FIGURE 10-3. Core-type induction furnace with V-shaped melting channels.

manual labor, and the avoidance of zinc fumes and "brass shakes" have made the electric furnace an important factor in improving the comfort, health, and safety of the workman.

The Ajax-Wyatt furnace[6], most widely used in brass melting, is shown in two transverse cross sections in Figure 10-3. The primary coil, interlaced with a laminated iron core, is surrounded by a secondary channel imbedded in refractory material having a V- or wishbone shape of restricted cross section and located at the bottom of the cylindrical hearth. Due to the pinch effect and other electromagnetic forces, the metal is vigorously circulated between the melting unit and the hearth. Thus, the new metal charged into the hearth is rapidly melted by heat conveyed by the liquid brass flowing from bottom to top. The hearth, as well as the secondary melting channels and the transformer and primary coil, is contained in a steel casing lined with insulating bricks and refractory material. The primary coil and transformer are provided with a blower for cooling. The furnace is charged through a top opening, and discharging is done by tilting the furnace around its discharge spout, located at one side of the furnace.

Variations of the Ajax-Wyatt furnaces with a circular instead of the V-shape channel loop have been built and operated in Europe[7].

Figure 10-4 shows the Ajax-Tama-Wyatt furnace[8] in two transverse cross sections. The basic principle is the same as described below. Two primary coils are provided instead of one, thus establishing a double loop

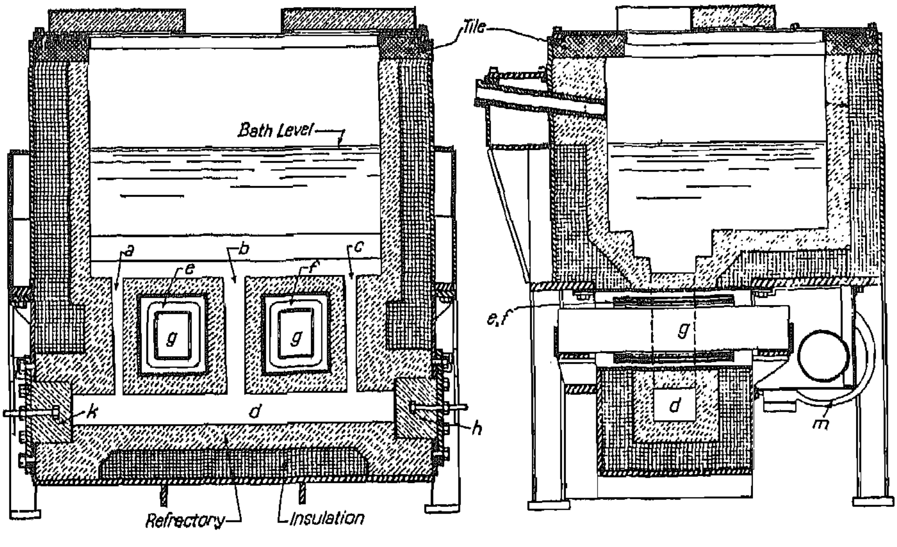

FIGURE 10-4. Core-type induction furnace with straight melting channels.

of melting channels around the two legs of the laminated transformer core. There are three vertical and one horizontal melting channels, all of straight shape, the horizontal channels having a much larger cross section than the others. With this construction, overheating in the bottom part of the inductor unit is greatly reduced. This type of furnace, though chiefly developed for melting aluminum, has shown equally beneficial results when applied to copper and copper alloys. In particular, the overheating of the metal and partial vaporization of zinc in the melting channels as previously observed in older types of furnace have been practically eliminated and the life of the melting channels has thereby been increased. In the earlier furnaces with channels of small cross section there was a tendency for gradual clogging of the channels, and many furnaces had to be relined not because the channels were worn out or eroded, but due to excessive clogging which resulted in diminished production. The inductor unit is provided with a windbox and two blowers which circulate air at high velocity by suction through the transformer assembly. The bottom channel can be inspected and repaired by opening the clean-out plugs.

Figure 10-5 shows two transverse vertical cross sections of the Ajax-Scomet furnace of 1,000 kw capacity[9]. The furnace consists of a hexagonal steel drum (*A*) provided with a refractory lining (*B*) of prefired shapes and bricks. Three detachable inductor units (*C, D, E*), each rated at 333 kw, are attached to the lower side of the drum, generating heat in the melting channels (*F, G, H, K*), which form two secondary loops interlaced with two primary coils (*L, M*) acting as a secondary winding of a short-circuited transformer. The two primary windings surround a closed transformer core (*N*). The construction of the inductor unit is identical with that in Figure 10-4.

The inductor units can be readily detached and replaced without interrupting the operation of the furnace. This is accomplished by rotating the drum to bring the inductor requiring changing above the molten metal line, thus discharging the inoperative inductor while keeping the metal heated with the two remaining inductors. In the case of the bottom inductor, it must be drained together with one of the lateral inductors while only one inductor remains filled with molten metal and delivers power to keep the residual metal in the drum in a molten condition.

The furnace drum has a large charging opening with dimensions of 2 by 3 feet, so that a 5,000-pound charge consisting of miscellaneous scrap and virgin metal can be introduced in one batch by mechanical means. Total holding capacity of the furnace is about 23,000 pounds of brass, of which only about 5,000 pounds is discharged about every half hour. When the new charge is introduced, it finds a cushion of molten metal of about 18,000 pounds protecting the furnace lining from damage and accelerating the melting rate. The reason for this is that the solid metal charged is immediately and fully surrounded by molten metal so that the dissolving action starts promptly. Figure 10-6 shows the discharge end of this furnace and the 5,000-pound ladle used to feed a continuous casting machine.

Copper Melting

The copper melting problems are quite different from those just explained for brass. Since copper is not a volatile metal, reduction of melting losses is only of secondary importance.

Copper cathodes are melted and cast into molds to obtain a shape suitable for further manufacture, *i.e.*, wirebars, cakes, billets, etc. Due to the inherent property of molten copper of absorbing gases from the combustion products, melting cathodes in reverberatory furnaces requires a full cycle of oxidation and deoxidation. What should be a simple melting process is thus expanded into a whole refining process.

Economic and metallurgical benefits expected from electric melting of cathodes as compared with reverberatory furnace practice can be summarized as follows:

(1) High uniformity of product. Castings produced from electrically melted copper exhibit unusual uniformity in respect to composition and physical properties.

(2) Freedom from contamination. Contamination of the melt in reverberatory furnaces by combustion products and extensive contact with iron blowing pipes and rabbling tools is avoided. The original high purity of the cathode copper is well preserved.

(3) Simplification. The reverberatory process requires years of training and experience not necessary in the electric melting process.

(4) Continuity of operation. The electric furnace is adaptable to continuous melting and casting in contrast to the batch-type operation of the reverberatory furnace.

(5) Power rates. In locations of cheap power rates electric melting is cheaper than fuel melting. This applies to Copper Cliff, Ontario, where electric melting was pioneered; Cerro de Pasco, Peru; East Montreal, Quebec; Garfield, Utah; Bolidens, Sweden; and other places where electric melting has been carried out commercially.

During the past twenty years considerable research and development work has been done in adapting the electric furnace to large-scale melting of electrolytic copper. Waddington and Bischoff[10] were the first to develop a successful process for arc melting, while Summey and Bahney[11] carried out the ground work on induction melting of copper cathodes.

Tama, in 1930[12], described a laboratory experiment melting 10 tons of cathodes and casting vertical wirebars from a 150-kw induction furnace of the same type as was used for melting brass, shown in Figure 10-3.

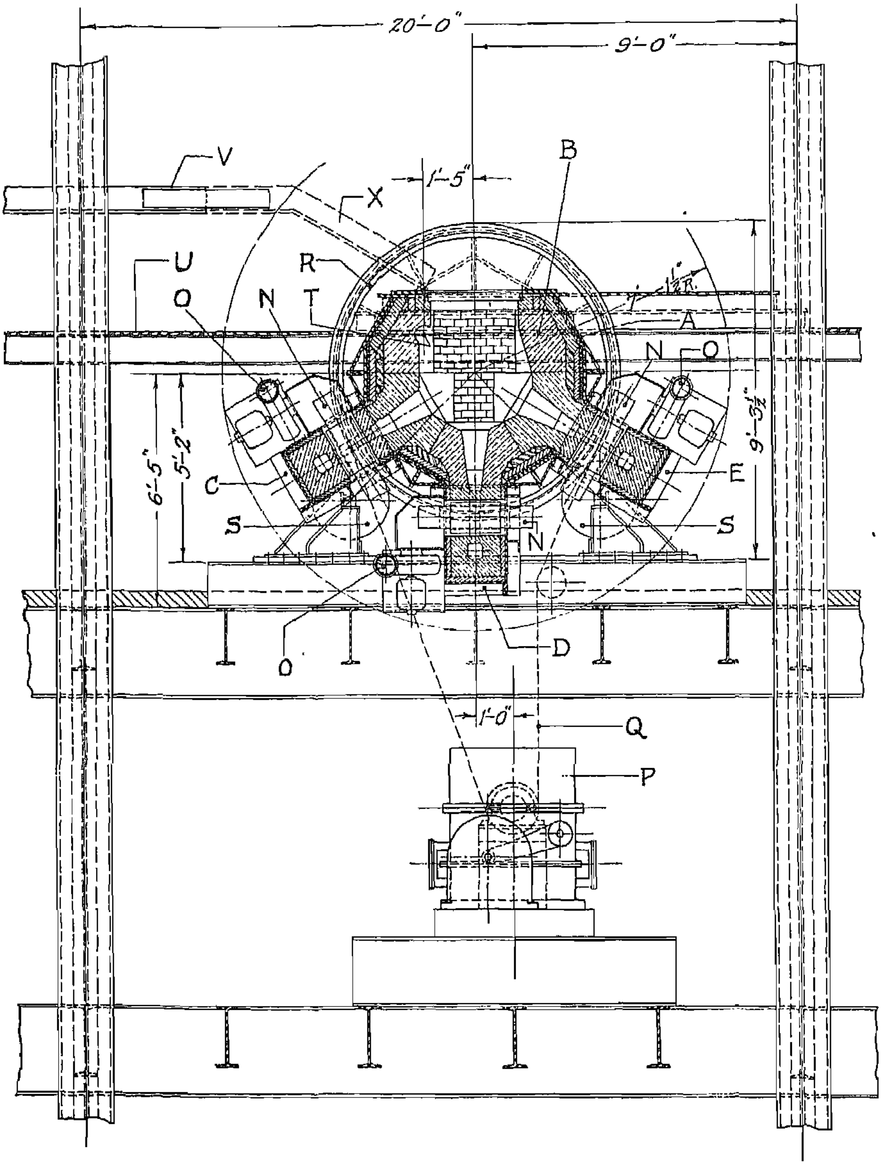

Figure 10-5. Drum-type three-phase induction furnace for melting brass, of 1,000-kw capacity.

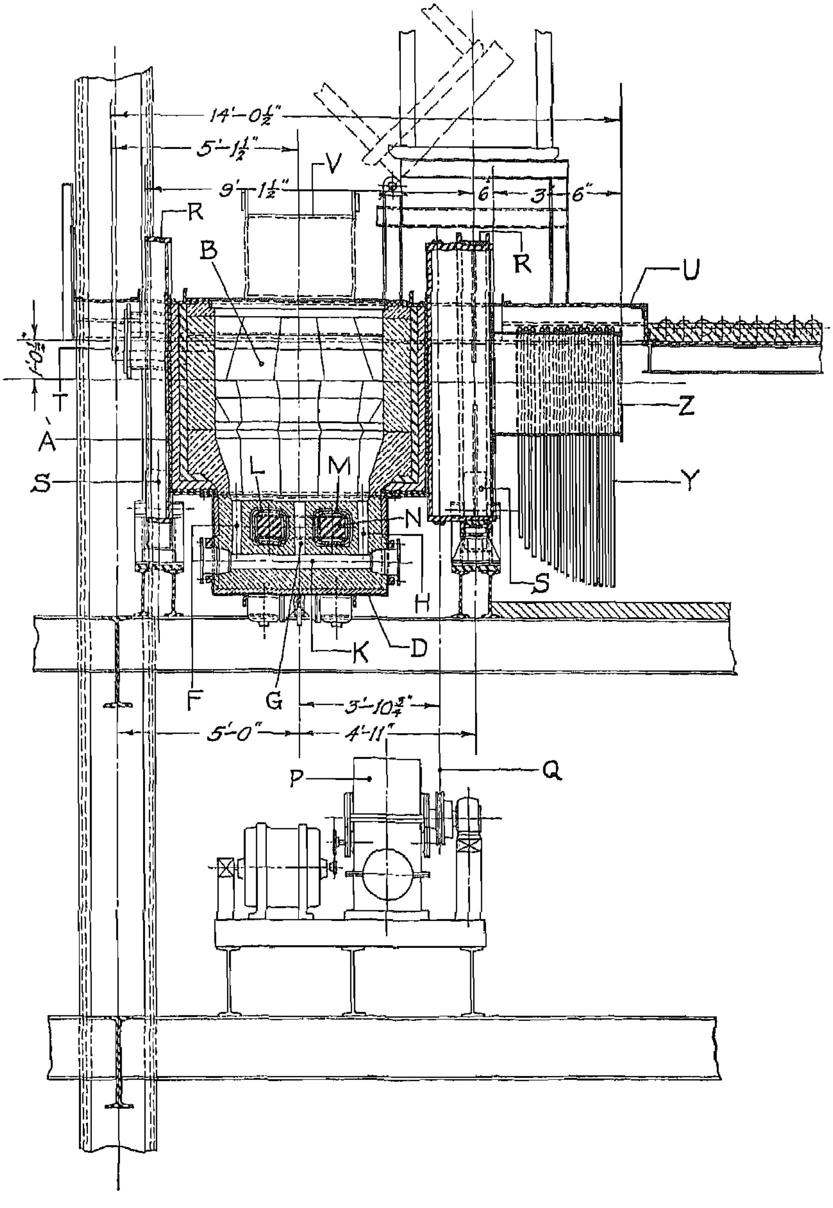

FIGURE 10-5. (*Continued*)

From all of these wirebars sound products were obtained by rolling and cold drawing; flaws in the wire which might be traceable to cracks in the wirebars were not observed. It was found that these wirebars were fully qualified for manufacture of wire; oxygen was not traceable.

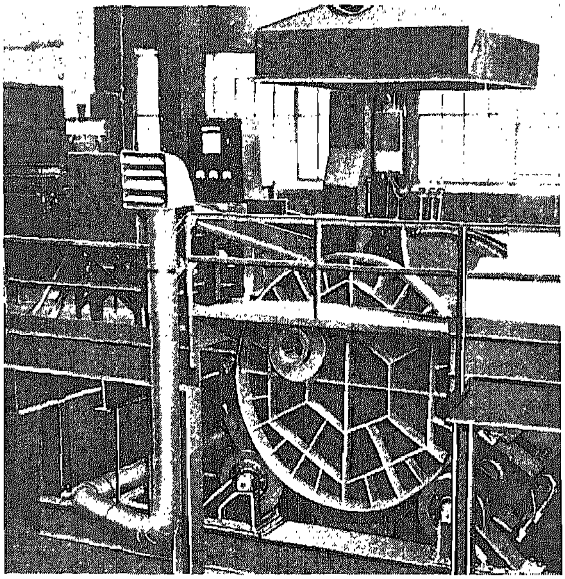

FIGURE 10-6. Discharge end of drum-type induction furnace, as shown in Figure 10-5.

Because of the possibility of operating the induction furnace at low temperature and with a protective atmosphere, the logical use of this type of furnace is for production of oxygen-free copper. Furthermore, because of the absence of cuprous oxide in the oxygen-free melt, the refractory linings of the induction furnace can be operated for longer periods of time without damage. The vulnerability of the induction furnace lining to attacks of cuprous oxide is the main reason why tough-pitch copper is melted only in arc furnaces.

The largest induction furnace ever built for melting and casting oxygen-free copper, shown in Figures 10-7 and 10-8, was started in 1929, at the U. S. Metals Refining Co., Carteret, New Jersey[13], and has produced thousands of tons of oxygen-free copper. It is the first large induction furnace to operate for the production of wirebars, billets, and cakes on a commercial scale. Before that time oxygen-free copper was hardly more than the result of a laboratory experiment. Since 1948, this furnace has operated in connection with a continuous casting machine.

The furnace has two chambers consisting of two steel cylinders, con-

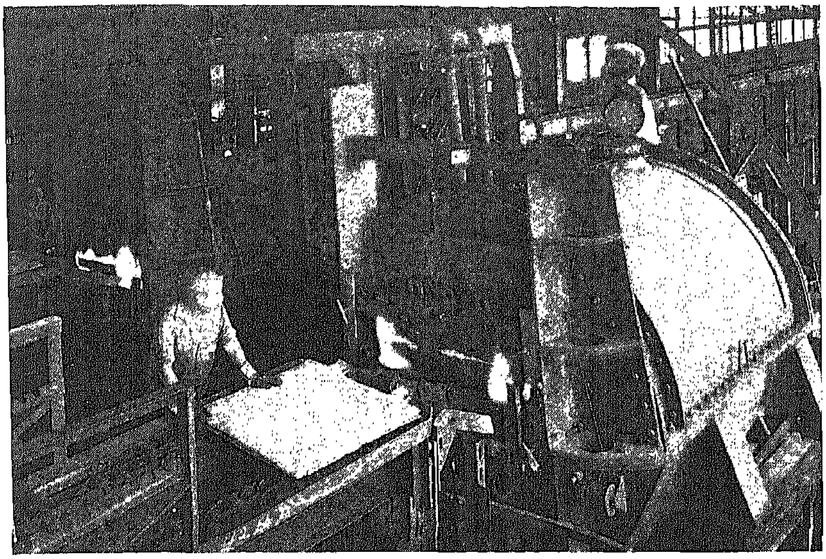

FIGURE 10-7. Charging end of 2,100-kw double-chamber oscillating induction furnace for melting copper.

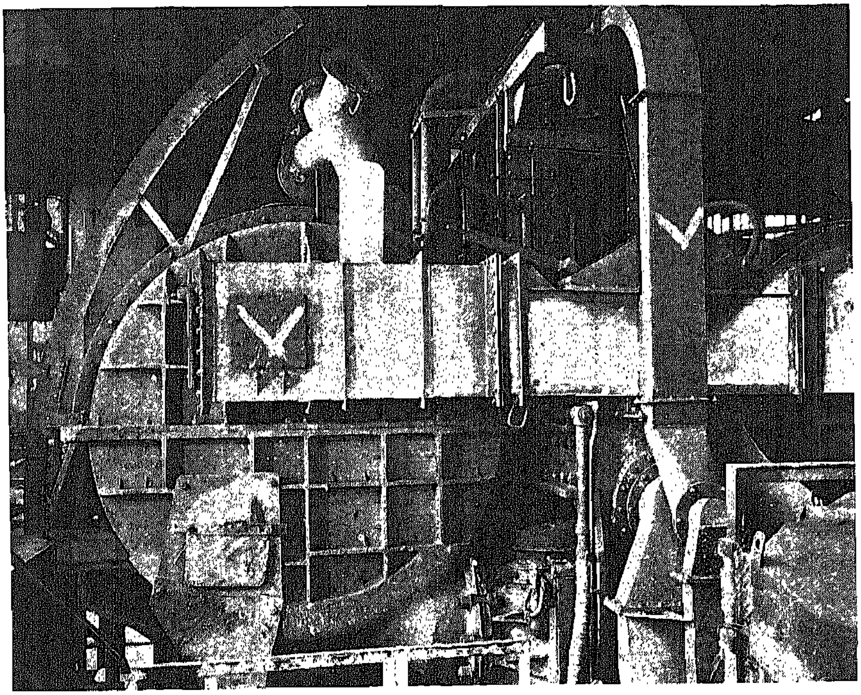

FIGURE 10-8. Discharging end of 2,100-kw double-chamber oscillating induction furnace for melting copper.

nected by melting channels interlinked with the inductor units. The two chambers are constantly oscillating about fifty times per hour to circulate copper through the secondary channels. This mechanical oscillation is necessary because the electromagnetic forces described above are not sufficient to dissipate the heat produced in the long, slender melting channels. The temperature of the copper in each chamber is automatically maintained by platinum-rhodium thermocouples and recording instruments. This furnace has a total maximum electric capacity of 2,100 kw and under normal conditions produces a total of 24,000 pounds of copper per hour, with a consumption of 223 kw-hr per ton of copper at full load with the temperature of the metal bath 1150°C (2100°F).

Figure 10-9 shows part of an installation for the production of oxygen-free copper at Outokumpu Oy in Pori, Finland[14]. The melting furnace shown in the upper left-hand corner is constructed in the shape of a drum, in principle similar to the one shown in Figure 10-5, with four inductor units, each of 150 kw capacity, having a total of 600 kw installed rating. The copper flows into a holding furnace shown on top of a casting wheel. The whole system through which the molten copper flows is kept under controlled atmosphere. The power consumption of this unit, including melting and holding furnace and standby power, is about 320 kw-hr per metric ton.

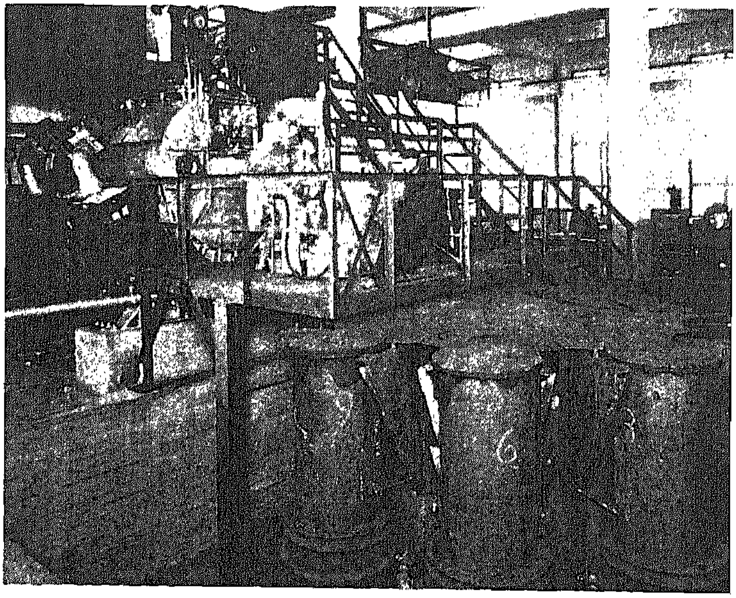

FIGURE 10-9. Drum-type induction furnace of 600-kw capacity for the production of oxygen-free copper, showing the casting wheel.

Induction furnaces are used extensively as holding units in connection with arc melting furnaces for the purpose of equalizing temperature and composition[15]. Figure 10-10 shows the drum-type induction furnace holding about 5,000 pounds of molten copper at the Canadian Copper Refiners Ltd. plant in Montreal, which is used for regulating the flow of molten copper into the casting wheel and is connected with the arc melting furnace by a short launder. The detachable inductor unit of the holding furnace is rated at 100 kw and is provided with automatic temperature control.

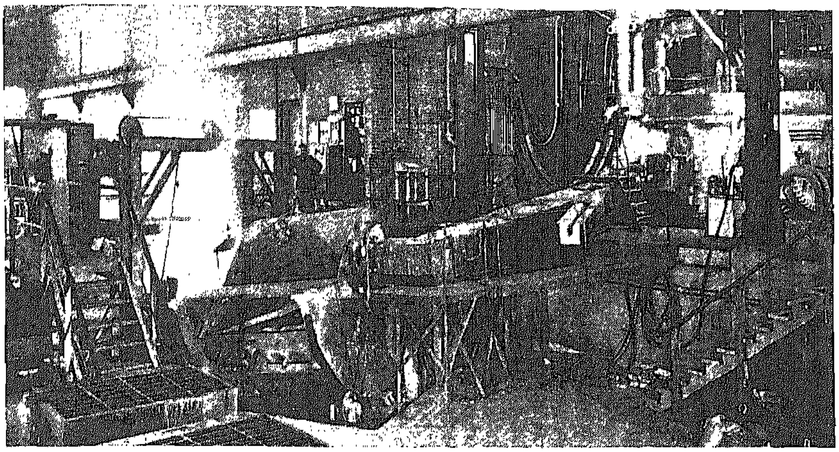

FIGURE 10-10. Induction holding furnace for casting tough-pitch copper, connected by a launder with an arc furnace.

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Chapter 11

Treatment of Electrolytic Copper Refinery Slimes

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The principal object of treating copper refinery slimes is the recovery and separation of precious metals. The original methods of treatment were relatively direct, but crude. With time, increasing attention has been paid to improvement in the recovery and quality of by-products, mainly selenium and tellurium. Whatever method is employed, the product is doré metal—a silver-gold alloy with or without metals of the platinum group.

Characteristics of the Slimes

Anode slimes are made up of those components of the anodes which are not soluble in the electrolyte. They contain varying quantities of copper, silver, gold, sulfur, selenium, tellurium, lead, arsenic, antimony, nickel, iron, silica, etc. Recent analyses of some anode coppers are given in Table 11-1. Comparative analyses of the raw slimes and treated slimes from these coppers are listed in Tables 11-2 and 11-3.

The color of raw slimes is normally grayish black and the particle size is minus 200 mesh.

Some of the copper in the slimes originates in the cuprous oxide of the anodes and is therefore dependent on the oxygen content of the latter:

$$Cu_2O + 2H_2SO_4 \rightarrow CuSO_4 + H_2O + Cu \qquad (1)$$

Opinions have been expressed that some of the copper is formed by decomposition of cuprous to cupric sulfate

$$Cu_2SO_4 \rightarrow CuSO_4 + Cu \qquad (2)$$

The product of either reaction is very finely divided metallic copper.

TABLE 11-1. COPPER ANODE ANALYSES

	A. S. & R.			Anaconda	Bolidens	C.C.R.		Cerro de Pasco	E. R. & S.	
	Baltimore	Perth Amboy	Tacoma	Great Falls		Domestic	Noranda		Normal	High Temperature
Cu	99.43	99.+	98.08	99.45	99.00	99.41	99.29	97.66	99.32	98.50
Ag*	18.7	55	90.20	46.72	36	46.00	32.54	188	10.62	26.30
Au*	1.41	1.5	3.59	.32	4.5	3.29	4.66	1.20	5.79	2.82
Se	.061	.07	.051	.012	0.2	0.13	0.14	.016	.022	.029
Te	.045	.02		.024	0	0.029	0.026	.010	.039	.025
As	.064	.06	.06	.059	.004	0.012	0.0007	.09	.08	.220
Sb	.031	.1	.198	.027	.015	0.075	0.0001	.39	.104	.310
Bi	.008	.002	.007	.003	.004			.01	.004	.006
Pb	.031	.1	.073	.024	.05	0.058	0.006	.30	.039	.183
Ni	.157	.2	.21	.028	.20	0.02	0.05	.025	.123	.251
Co										
Fe	.0017		.071	.0028	.003	0.0012	0.0009	.02	.009	.022
S		.005	.011	.0016	.015	0.0063	0.0061	.029		
Sn										
Zn				.0025	.015			.007		
Insol.					.005				.05	.058
CaO										
O					.25			.50		

TABLE 11-1. COPPER ANODE ANALYSES (Cont'd)

	Mt. Lyell	International Nickel	Kennecott	Norddeutsche	Phelps Dodge		Outokumpu	Raritan	Rhodesia	U.S. Metals
					El Paso	Laurel Hill				
Cu	99.22	99.22	99.28	98.9 -99.1	99.6	99.3-99.5	99.04	99.491	99.78	98.90
Ag*	4.00		17.138	19.84 -30.13	5-20	5-15	10.29	8.673	2.37	46.18
Au*	.77		1.523	.42 - .64	0.1-0.7	0.25	0.43	0.232	.018	
Se	.015	.05	.047	.04 -.06	.02	.01-.03	.017	.035	.0143	.044
Te	.0058	.007	.022	.002 -.006				.008	.0006	.018
As	.0026	.007	.062	.09 -.20	.003	.02-.04	.008	.038	.0018	.03
Sb	.0047	.0015	.023	.023 -.11	.001	.01-.05	Tr.	.024	.0003	.05
Bi	Tr.	.001	.004	.0033-.0042			.002	.002	.0061	
Pb	.009	.006	.035	.11 -.17	.01	.02-.06	.0046	.045		.21
Ni	.012	.50	.075	.24 -.34	.03	.06-.15	.71	.043	.0161	.22
Co	Tr.						.0004		.0055	
Fe	.045	.0010	.014	.03 -.10	.002	.003	.014	.008	.0035	.002
S	.14		.006				.005	.007		
Sn				.007 -.010			.0008	.014		.043
Zn	Tr.						.0035	.002		.004
Insol.	.075		.046				.002			
CaO	.076									
O			.22	.15			.18	.269		

* Ounces per ton.

TABLE 11-2. RAW SLIMES ANALYSES

	A. S. & R.			Anaconda	Bolidens	C.C.R.	Cerro de Pasco	Australia		International Nickel	Kennecott	Outokumpu	Raritan	Rhodesia
	Baltimore	Perth Amboy	Tacoma	Great Falls				E. R. & S.	Mt. Lyell					
Cu	26.68	20		19.3	40		2.74	16.91	75.62	25.40	26.4	11	24.27	35.53
Ag, o.p.t.	3,067	6,000		8,837	3,300	4,860	7,738	1,310	258		4,428	2,800	2,174	1,857
Au, o.p.t.	223			76	450	505	49	481	48		404	150	56.85	13.9
Se	9.65	7.5		3.4	21	18.28	0.64	2.70	2.01	13.20	11.59	4.33	8.30	14.49
Te	7.34	1.5		8.1	1	4.26	0.45	0.98	0.33	1.80	4.84		2.39	1.06
As	3.78	5.0		5.1	0.8	0.26	2.80	9.75	.05	0.45	1.40	0.70	3.94	0.29
Sb	3.10	4.0		4.2	1.5	0.48	16.00	17.00	.40	0.15	0.49	0.04	5.29	0.06
Bi	0.25	0.7		0.2	0.8		0.47	0.52	Tr.		0.14			0.48
Pb	5.15	12.0		4.6	10	4.73	13.80	6.50	.30	2.25	8.64	2.62	14.53	.91
Ni	0.49	1.0		0.17	0.5	0.10		2.20	.09	6.65		45.21	0.34	.27
Co					.02				Tr.					.09
Fe	0.08	1.5		0.07	.04		2.10		.23	0.12		0.60		1.42
S		4		2.0	3.5	2.64	5.10	4.6	11.15	7.25		2.32		6.55
Sn		0.7										1.00		
Zn				0.10	<1		0.40		Tr.			Tr.		
Insol.		1.0 (SiO_2)			0.3	4.14 (SiO_2)	16.30 (SiO_2)		1.20			2.25		6.93
CaO		0.7			0.05									0.54
Al_2O_3		0.6					0.90					Tr.		1.03

TABLE 11-3. TREATED OR LEACHED SLIMES ANALYSES

	A. S. & R.		Anaconda	Bolidens	C.C.R.	E. R. & S.	International Nickel	Norddeutsche	Phelps Dodge		Outokumpu	Raritan	U.S. Metals
	Perth Amboy	Tacoma	Great Falls						El Paso	Laurel Hill			
Cu	1.0	1.77	1.59	1.5			1.50	2-3	1-2	1-2	0.53	2.16	1.85
Ag, o.p.t.	7,875	8,637	11,785	8,490	10,740	3,000		3,266-4,083	7,000	2,500	10,750	3,664	7,390
Au, o.p.t.		407	108	1,320	1,000	1,250		*52.2 -68.0*	*200*	*0.80*	565	96	406
Se	10.0	5.30	4.6	2.0	5.8		20	6.2 - 7.7			12.92*	12.07	7.03
Te	2.0		10.4		7.7		2.50	0.6 - 0.9	12	4		2.61	1.56
As	0.8	3.16	3.5		0.76		.05	3.6 - 3.9			0.31	1.69	1.07
Sb	5.3	16.91	6.3	4.4	0.9		.15	8.5 - 9.9	0.5	1	0.21	8.57	5.42
Bi	0.9	0.49	0.4	2.3				0.55- 0.80	1	3			0.34
Pb	16.0	7.1	6.1	30.0	9.47		10.0	18.5 -22.6			11.76	23.20	27.31
Ni	*0.1*	*0.42*	*0.23*	*0.7*	0.04		1.0	0.85- 1.60	5	12	0.85	0.24	0.87
Co								.17-.25					
Fe	0.3	3.58	0.11		0.08		.07				0.3		
S	5.4		2.6		2.3			7.0 - 7.4					
Sn	*0.9*	Tr						2.05- 2.3			*1.27*		4.29
Zn			0.13										
Insol.	1.3		3.5	1.9	9.87 (SiO_2)				8 (SiO_2)	17 (SiO_2)	13.26		
CaO	0.9												
Al_2O_3													

* No. 2 leached slimes before *selenium removal.*

Much of the copper and silver is combined with sulfur, selenium, or tellurium, the amount so combined depending on the composition of the slimes. Apart from copper and the platinum group elements the only slimes component existing in uncombined state is gold, although it may be partly combined with tellurium and to some extent alloyed with silver.

At room temperature the slimes are not appreciably oxidized and in absence of air they are unaffected by dilute sulfuric or hydrochloric acid, though readily attacked by dilute nitric acid. In the presence of air, copper is slowly dissolved by dilute sulfuric acid with the liberation of selenium and tellurium. The rate of the reaction increases with temperature. The liberated tellurium may be partly oxidized and dissolved by hot dilute sulfuric acid.

When heated in air the slimes are oxidized with the formation of the corresponding oxides, selenites, and tellurites. Selenium and tellurium oxides are also formed and may be partly volatilized.

On heating the slimes with strong sulfuric acid, oxidation and sulfation take place. Silver, copper, and other base metals are sulfated; gold is unaffected, while selenium and tellurium are oxidized to the corresponding oxides or oxysulfates. On raising the temperature to that of roasting, the oxysulfates decompose and selenium dioxide is driven off.

Treatment of Slimes Components

Direct smelting of slimes is no longer practiced, since excessive formation of matte and slag causes heavy recirculation of precious metals, especially of silver. A more satisfactory approach is separating the component elements one by one. In this manner they may be recovered in a reasonably pure state, permitting either immediate withdrawal from the circuit or recirculation with a reduced number of steps in the treatment.

The most favored procedure is the removal of copper and then of selenium and tellurium. Other elements, apart from precious metals, are normally not recovered, except for lead, and that only in the close proximity of a lead smelter. The end product is doré metal containing a small quantity of copper and minor amounts of other impurities, and sometimes metals of the platinum group.

In an ideal process the various impurities would be recovered in a pure state separately, as early and as completely as possible, so as to leave little refining to be done in the doré or cupelling furnace, with minimum consumption of fuel and fluxes and minimum formation of matte and slags. In practice many compromises must be made, mainly because no element is removed entirely and because more than one element is usually removed at any one time.

Removal of Copper. As a rule, copper is removed as a water-soluble sulfate. In this form it may be sent directly into the electrolyte circulation system; however, due to the presence of impurities, such as selenium and tellurium, this is practiced in few instances only. The leach solution is worked for the recovery of copper as copper sulfate or elemental copper.

Following are the commercial methods for recovering copper:

Oxidizing Roast[2, 3, 5]. Shallow layers of slimes are heated to 250 to 425°C (500 to 800°F). Sufficient air is admitted both to effect oxidation and to hold the temperature below the fritting point. The bed is generally rabbled to reduce the time of roasting. Copper compounds are broken down and together with free copper form copper oxide, selenite, and tellurite. Some selenium and arsenic are volatilized. The calcine is leached with dilute sulfuric acid. The copper solution is then treated to recover copper sulfate or elemental copper.

The main objections to roasting are dusting, which introduces recirculation, mainly of selenium; only partial elimination of the more volatile impurities; and an impure leach liquor containing selenium and tellurium.

A variation of this method consists of heating slimes mixed with fine soda ash; this will be described under Removal of Selenium.

Sulfatizing Roast[1, 4, 6, 10, 11]. This method is an improvement over air roasting in that concentrated sulfuric acid is added to the slimes prior to charging or during the roast by spraying, the acid acting both as an oxidizing and a sulfatizing agent:

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + 2H_2O + SO_2 \qquad (3)$$

Other metallic components react similarly. Selenium and tellurium are oxidized to the corresponding dioxides or oxysulfates:

$$Se + 2H_2SO_4 \rightarrow SeO_2 + 2H_2O + 2SO_2 \qquad (4)$$

$$Te + 2H_2SO_4 \rightarrow TeO.SO_3 + 2H_2O + SO_2 \qquad (5)$$

Since the acid is required both for oxidation and for sulfation of the copper, the amount necessary is double that used in the methods described under Oxidizing Roast and Aeration in Dilute Sulfuric Acid.

Roasting at high temperature drives off the selenium dioxide. To prevent decomposition of copper sulfate, the temperature must not exceed 650°C (1200°F).

The roasting step may be modified by a preliminary heating of the slimes-acid mixture below the boiling point of the acid[6, 10, 11]. The sulfur dioxide and water given off and the base-metal sulfates formed increase the porosity of the mix and aid in retaining the acid needed to complete the oxidation of selenium and tellurium at a higher temperature. Roasting then merely drives off the volatile oxides.

The roasted slimes are leached with hot water. The leach liquor carries much silver and some selenium and tellurium. Silver is readily cemented on metallic copper. Selenium requires a somewhat longer time for cementation, while tellurium is more resistant to cementation than selenium.

The cementation reactions involved are complex, but may be represented by the over-all equation

$$4Cu + 2H_2SO_4 + H_2SeO_3 \rightarrow 2CuSO_4 + Cu_2Se + 3H_2O \qquad (6)$$

Aeration in Dilute Sulfuric Acid. In this method the slimes suspended in hot dilute acid are blown with air. Copper may be reduced to a fraction of 1 per cent. The process is economical of reagent, using one mol of acid per mol of copper. The saving in acid and also in fuel is partly offset by the cost of steam. The equipment required is simple, though bulky. The time required to bring the copper to 0.5 per cent depends on the initial copper content and on the copper compounds present.

In a patented variation, ferric sulfate is added toward the end of the treatment to hasten dissolution:

$$Cu + Fe_2(SO_4)_3 \rightarrow CuSO_4 + 2FeSO_4 \qquad (7)$$

$$2FeSO_4 + H_2SO_4 + \tfrac{1}{2}O_2 \rightarrow Fe_2(SO_4)_3 + H_2O \qquad (8)$$

Any solution containing free acid may be used in this method. Silver is not dissolved, but the selenium and tellurium combined with copper are set free. Some of the tellurium is oxidized and dissolved in the hot acid solution, making the latter unsuitable for return to the electrolytic copper department. When sufficient silver is present in the slimes to combine with all the tellurium and selenium, the tellurium does not dissolve in the dilute acid.

Copper sulfide and nickel oxide are not affected by dilute acid aeration, and require treatment with concentrated acid as outlined later.

Pyrometallurgical Methods. Direct smelting, one of the earliest methods, is no longer used unless the copper content is very low. Methods like smelting, scorifying, and cupelling are reserved to the end of the treatment, after most of the impurities have been removed by a combination of roasting and leaching methods.

Removal of Selenium. Wherever selenium occurs in appreciable quantities, its market value makes recovery attractive. The most important methods of recovering selenium are smelting with soda and niter, roasting with soda, and roasting with sulfuric acid.

Soda Smelting[5, 6]. This is a pyrometallurgical method. The raw slimes are first decopperized by any method described earlier. In a few refineries adjoining a lead smelter, the lead is removed by cupellation. Elsewhere the treated slimes are smelted in a doré furnace.

The slimes as charged are mixed with soda and silica. The first slags are mainly siliceous and contain such impurities as iron, arsenic, antimony, and lead. The molten charge is then blown with air to oxidize and volatilize as much as possible of the arsenic, selenium, and tellurium. The soda slags that follow are high in selenium and tellurium. The melt is then rabbled with niter to oxidize the copper and make it amenable to slagging.

The soda slag is crushed and leached with water and the filtered liquor neutralized with sulfuric acid or acid-bearing scrubber solutions to pH 6.2 to precipitate tellurium as tellurous acid. The filtrate is then gassed with sulfur dioxide to precipitate selenium. Not all the tellurium is precipitated on neutralizing, and eventually it appears in the refined selenium as a persistent impurity.

Replacing soda ash with solid caustic soda improves the efficiency of the process, but increases corrosion of the furnace lining.

Scrap iron has been used in addition to the soda to break down the matte into soda slag and bullion. No blowing was required. Cost of reagents and time of processing were markedly reduced. However, formation of a sodium selenide slag made selenium recovery more complicated.

Treatment with niter tends to oxidize selenium to selenate, which is not easily reduced by sulfur dioxide. However, niter is needed to break down the copper matte, but its addition should be left toward the end of the refining period after the bulk of the selenium has been removed with soda. Selenates are reduced in the presence of hydrochloric acid, but chloride ions are not desirable in lead-lined equipment and require rubber or plastic lining.

Japanese methods employ smelting the slimes with metallic lead and alkalies, the noble metals combining with the former and selenium with the latter.

Soda Roast. A modification of the pyrometallurgical method is the roasting or baking of raw or decopperized slimes intimately mixed with fine soda. The temperature must be kept below the sintering point to assure access of air essential to good elimination of selenium. The charge may be rabbled during heating. Selenium is recovered from the calcine water-leach liquor by either of two methods[8].

In the first method, the liquor is neutralized to precipitate tellurium and then treated with sulfur dioxide, preferably in the presence of hydrochloric acid.

The second method is used where the tellurium content is negligible. The leach liquor is evaporated to dryness and the sodium selenite and selenate are reduced with coke to selenide[9].

$$Na_2SeO_3 + 3C \rightarrow Na_2Se + 3CO \qquad (9)$$

This is redissolved and blown with air to precipitate selenium and regenerate hydroxide, which is carbonated and returned to the process.

$$Na_2Se + H_2O + \tfrac{1}{2}O_2 \rightarrow 2NaOH + Se \qquad (10)$$

With proper roasting, recovery of selenium may be 95 per cent and over.

Any tellurium present in the slimes is similarly affected, forming a water-soluble sodium tellurite. For this reason, soda roasting is not feasible with high-tellurium slimes or where recovery of high-purity selenium is desirable.

The water-leached slimes may be leached with dilute sulfuric acid. Good removal of copper is thus achieved.

Sulfuric Acid Roast. On oxidizing roasting of slimes, some selenium is driven off as dioxide or in elemental state and is recovered in the scrubber system. Elimination of selenium is poor, the dust losses are high, and the scrubber mud is impure and is usually returned to the process.

Much improvement is obtained with a sulfating roast as described in the section under Removal of Copper. The slimes are mixed with acid prior to roasting. The mix is digested before charging into the roaster. Selenium dioxide is collected in the wet scrubber-Cottrell system, the combustion gases being led to a separate scrubber system.

Removal of Tellurium. Tellurium is eliminated from the slimes as a water-soluble sodium tellurite. It is converted into this form after a preliminary oxidizing or sulfatizing treatment. This may be done in several ways: (1) roasting or baking a slimes-soda mix (this is a combined oxidizing and "alkalizing" treatment); (2) refining with soda in a doré or cupelling furnace; (3) boiling the slimes with caustic soda after an oxidizing or sulfating roast.

Sodium tellurite is extracted by water leaching the roasted product of (1) or the soda slag from (2). In all three cases, the liquor also contains sodium selenite. Boiling the sulfate-roasted slimes extracts some lead in addition to selenium and tellurium.

Whatever the method, the aqueous solution is neutralized to pH 6 to 6.2 to precipitate tellurium dioxide, or tellurium mud. This is purified by redissolving in caustic soda, precipitating the impurities with sodium sulfide or sodium sulfite, and neutralizing again to obtain tellurium dioxide of higher purity. In a method formerly used, the mud containing copper and selenium as impurities was roasted with sulfuric acid to volatilize the selenium and then water-leached to remove the copper.

There are three methods for recovering elemental tellurium from the mud: (1) direct reduction by heating with flour under a borax cover; (2) dissolving the mud in hydrochloric acid or in sulfuric acid to which some salt is added, followed by reduction with sulfur dioxide, filtration, washing, drying, and melting; (3) dissolving the mud in caustic soda and electrolyzing with iron anodes and stainless steel cathodes[12]. The last method appears to be the most attractive of the three.

Parting and Recovery of Silver and Gold. As noted earlier, the main purpose of a slimes treating process is the production of doré metal. At one time doré metal was cast in thin sheets and boiled with sulfuric acid. The silver sulfate solution was diluted and silver recovered by precipitation on copper. The silver bullion assayed about 998 to 999 fine and always carried some gold and copper.

The two electrolytic methods which have displaced acid parting are the Moebius, employing vertical electrodes, and the Thum-Balbach, with horizontal electrodes. Examples of both are given in the latter part of this chapter.

Silver is deposited on the cathodes in the form of loosely adhering crystals which are washed and melted into bars assaying 999.8 to 999.9 fine. The anode mud may contain one-third silver and two-thirds gold. It is boiled with sulfuric acid to dissolve silver and other impurities and to bring up the fineness. Lead and tellurium are not easily removed by boiling with acid and care must be taken to eliminate them in doré furnace refining.

Should platinum group metals be present in sufficient quantity, the gold is refined electrolytically by the Wohlwill process. An example of this is also described below. Electrolytic gold is 999.7 to 999.9 fine.

The treatment of the platinum-group metals is outside the scope of this chapter.

Silver Refinery Practice

The quantity of raw slimes produced per ton of electrolytic cathodes deposited varies widely from 2.8 pounds per ton for Nkana, Northern Rhodesia, to 50 pounds per ton at Cerro de Pasco, Oroya, Peru, and is dependent on the composition of anode copper electrolyzed.

No single treatment is applicable to all raw slimes; the treatment is modified to suit their analysis. The following descriptions of methods used by six refineries cover all the main classes of slimes treatment presently in use throughout the world.

The analyses of anodes, of the corresponding raw slimes, and of the treated or leached slimes before their reduction to doré metal are given in Tables 11-1, 11-2, and 11-3, respectively.

Bolidens Gruvaktiebolag, Rönnskar, Sweden. Bolidens Mining Co. produces slimes of high selenium-low tellurium content (21 per cent Se, 1 per cent Te). Because of this combination, the first step in the flow sheet is a soda-ash roast, which is followed by a water leach to eliminate the selenium.

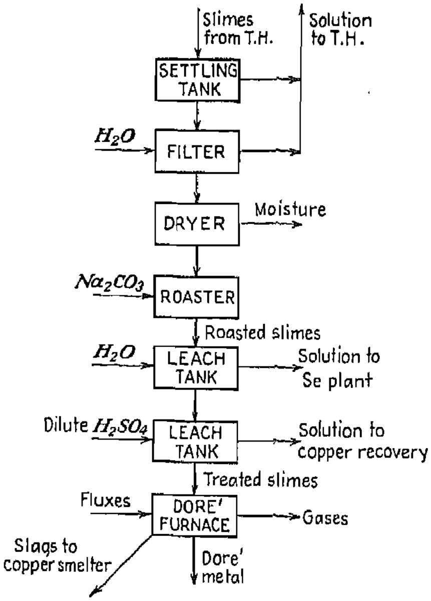

FIGURE 11-1. Bolidens Gruvaktiebolag silver refinery flow sheet.[7] (*Courtesy of the American Institute of Mining and Metallurgical Engineers.*)

0.45 ton Na_2CO_3 is mixed per ton of dried raw slimes. The mixture is roasted in a small multiple-hearth furnace at a maximum temperature of 450°C (840°F). The soda-baked calcine is water-leached in propeller-agitated tanks to remove selenium. The leach solution as press-filtered contains about 52 grams Se per liter and 32 grams Na_2CO_3 per liter. This solution is treated for recovery of selenium.

The copper contained in the slimes is oxidized during the soda roast and is removed by leaching with weak sulfuric acid, following the water leach. Normally 0.78 ton of concentrated sulfuric acid is required per ton of dry raw slimes. The acid extracts most of the copper. The solution containing about 62 grams Cu per liter is sent to insoluble anode tanks for recovery of copper.

The treated slimes contain only 2 per cent copper and 2 per cent selenium and are smelted in an oil-fired doré furnace in the usual way with a flux of 140 pounds of soda ash and 80 pounds of borax per ton of slimes charged.

The doré metal containing 858 parts silver, 106 parts gold, 25 parts copper per thousand is cast into anodes for parting in Moebius cells.

Canadian Copper Refiners Limited, Montreal East, Quebec, Canada. C.C.R. slimes are characterized by high selenium and tellurium content (18 to 20 per cent and 3.4 per cent). The raw slimes are filtered on an Oliver continuous filter and dried to 5 per cent moisture in an 8-foot diameter six-hearth oil-fired Herreshoff furnace.

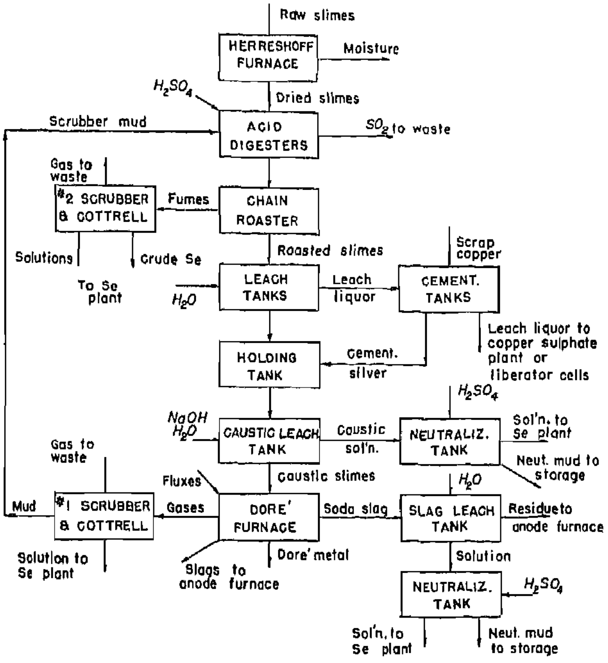

FIGURE 11-2. Canadian Copper Refiners Limited silver refinery flow sheet.

The dried slimes are charged in batches of 500 pounds to the acid digesters. Sufficient acid is added at the same time to produce a mix of good fluidity. The mix is digested at 150 to 230°C (300 to 450°F), depending on the stage of digestion. One pound of raw slimes containing 32.90 per cent insoluble Cu, 16.70 Ag, 20.93 Se, and 3.76 per cent Te requires 1.74 pounds of 100 per cent sulfuric acid. In practice, 20 per cent excess acid is used.

The digested slimes-acid mix is fed by a screw conveyor directly onto the pans of the chain roaster. The thickness of the slimes bed is normally ¾ inch at the start of roasting.

Essentially, the chain roaster installation consists of a furnace built around a pan conveyor on which the slimes-acid mix is roasted to volatilize the selenium. The effective roasting area of the slimes bed in the roaster is 92 sq feet. The temperature of roasting is maintained at 480 to 600°C (900 to 1100°F). With a roasting period of 45 minutes, the chain roaster production is 12,000 pounds of well-roasted product per 24 hours.

Near the discharge end of the furnace, a spiral cutter loosens the roasted cake from the pans, and the roasted slimes discharge into dump-bottom hoppers.

The roaster fume is drawn to the selenium scrubber system. Scrubber solution is pumped through sprays in the towers to humidify the gas prior to Cottrell precipitation and to recover the greater part of its selenium, selenium dioxide, and sulfuric acid content. The roasted slimes discharged from the chain roaster analyze: total Cu 21.9 per cent, water-insoluble Cu 1 per cent, Se 1.0 per cent, Te 2.2 per cent, Ag 2,800 oz. per ton, Au 260 oz. per ton. Elimination of selenium during roasting is about 93 per cent.

Countercurrent water leaching and decantation are employed to dissolve water-soluble copper sulfate. Dissolved silver in solution is precipitated in a separate tank on copper anode scrap. The cemented silver is combined with the water-leached slimes. About 20 per cent of the tellurium in the roasted slimes remains dissolved in the water-leach liquor after cementation on scrap copper.

The water-leached slimes are leached with 10 per cent caustic soda solution. An additional 50 per cent of the tellurium originally present in the roasted slimes is removed by the caustic treatment, increasing the over-all extraction to 70 per cent. Simultaneously, 40 per cent of the lead content is similarly removed, probably as sodium plumbite.

The caustic leach liquor is neutralized with sulfuric acid to remove tellurium and lead from the plant cycle as a tellurium mud which is held for tellurium recovery.

Caustic-leached slimes containing Cu 4.5 per cent, Ag 11,900 oz. per ton, Au 1,200 oz. per ton, Se 3.5 per cent, Te 6.5 per cent are melted in an oil-fired reverberatory-type doré furnace, with a hearth area of 34 square feet and an uptake area of 5.5 square feet. The furnace is charged with 12,000 to 15,000 pounds of slimes containing 30 per cent moisture and mixed with fine soda and silica. When the charge is completely molten, a siliceous slag containing most of the arsenic, antimony, and iron is skimmed off and returned to the copper-anode furnace. The charge is blown with air, lime being used as a flux. A slag of high lead content is next skimmed off and also returned to the anode furnace. Fused soda ash is then fed to the furnace, and the charge is blown with compressed air. The soda slag formed contains most of the selenium and tellurium from the charge as water-soluble sodium selenite and tellurite. This slag is leached with water, and the residue is returned to the anode furnace. The alkaline slag-leach filtrate is neutralized with sulfuric acid to precipitate tellurium. Selenium remains in solution and is recovered at the selenium plant. The neutralized mud is held for tellurium recovery.

The final stage of doré furnace refining is the removal of the residual copper by rabbling the charge with niter. This copper slag is returned to the anode furnace. The doré metal containing about five parts copper per thousand is ladled into water-cooled anode molds and is parted in Moebius cells.

The gases leave the doré furnace, pass through a flue for cooling and removal of much of the flue dust, and are then exhausted to the scrubber-Cottrell system.

Cerro de Pasco Copper Corporation, Oroya, Peru. Cerro de Pasco slimes are high in antimony and lead (see Table 11-2). Copper is 2.74 per cent before decopperizing and 1 to 1.25 per cent in treated slimes.

Both a copper refinery and a modified Betts electrolytic lead refinery are operated at Oroya.

The dried Betts and copper refinery slimes are mixed and smelted together in an oil-fired reverberatory furnace. Lead and antimony pass into the slag and baghouse dust and are retreated to produce antimony or antimonial lead, as required. A large proportion of the slag is at times returned to the lead blast furnace to ensure 2.5 to 4.0 per cent antimony in the lead anodes to the Betts plant. This produces an adherent slimes layer on the anode scrap and very pure lead cathodes from impure lead bullion (93 to 95 per cent lead).

The metal from the reverberatory melting furnace is scorified in converter-type furnaces. Here arsenic, antimony, and most of the lead are eliminated. The slag at this stage contains lead, antimony, and some bismuth and is returned to the melting furnace. When the metal reaches about 35 per cent silver content, it is transferred to one of the two cupel furnaces. All fume and dust from these operations is caught in a baghouse and treated for recovery of antimony and other metals.

In the cupel furnaces the metal is refined to 90 per cent silver content.

It is then treated with soda ash and niter to remove tellurium. At 98 to 99 per cent silver the metal is treated again with niter to remove the remaining base metals. The cupel furnaces are equipped with a separate baghouse installation. Cupel slags are treated for recovery of bismuth and silver. Soda and niter slags are treated in the tellurium plant for recovery of base metals and of tellurium as oxide. In general, the slags are returned molten to the preceding furnaces and finally leave the slimes melting furnace carrying very little silver, gold, and bismuth.

The doré anodes assaying 99.2 per cent silver are parted electrolytically. The gold mud is treated with sulfuric acid and melted to 993 to 995 fine gold, which goes to the Peruvian Mint.

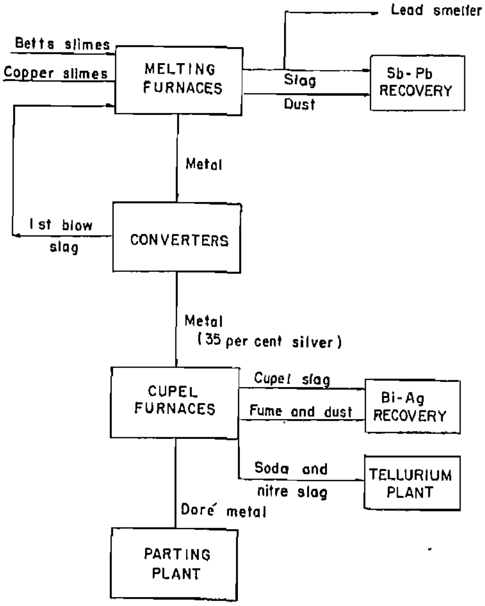

FIGURE 11-3. Cerro de Pasco silver refinery flow sheet.

The Electrolytic Refining & Smelting Co. of Australia, Proprietary, Ltd., Port Kembla, New South Wales. The Electrolytic Refining & Smelting Co. treats the slimes from the copper refinery at the Mount Lyell Mining & Railway Co., Ltd., Queenstown, Tasmania, as well as the slimes from its own anodes. Mt. Lyell slimes contain much copper sulfide, which necessitates roasting to the oxide, since copper sulfide is insoluble in sulfuric acid. Mt. Lyell slimes if treated alone tend to frit when roasted due to high copper content (67 per cent). On the other hand, the Electrolytic Refining & Smelting Co. slimes do not settle readily when leached alone. For these reasons, it is preferred to mix the slimes before treatment.

A coal-fired reverberatory furnace, with two superimposed hearths, 19 feet 6 inches by 9 feet 0 inches, is used for roasting. The combustion gas passes over the top roasting hearth and under the bottom drying hearth.

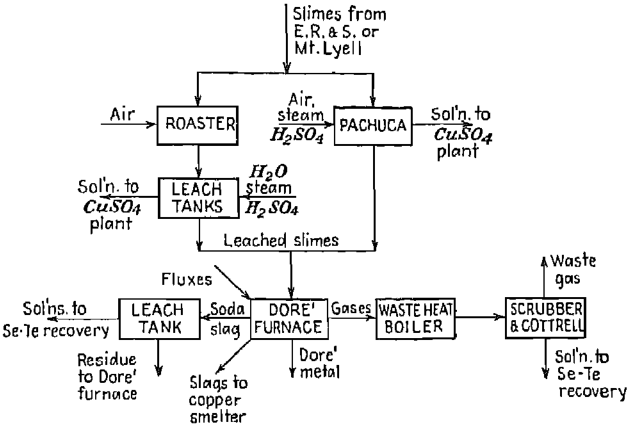

FIGURE 11-4. Electrolytic Refining & Smelting Co. of Australia silver refinery flow sheet.[7] (*Courtesy of the American Institute of Mining and Metallurgical Engineers.*)

Depending on their composition, the slimes are roasted from 14 to 24 hours. At completion of the roast, the slimes charge is quenched with water to prevent fuming and dusting and is raked from the roaster into portable hoppers for charging into the leaching tanks. The necessary solution is first charged to the tanks, and then sulfuric acid is added. Live steam is used for heating, and agitation is continued for 2 hours, sufficient to dissolve all the copper. Sodium chloride is used to precipitate any soluble silver. The solution is settled and decanted through a filter box to the copper sulfate plant.

The leached slimes are then filtered and dried on the lower hearth of the roaster, bagged, and stored until sufficient are accumulated for a doré furnace campaign. The leached slimes contain about 2 per cent Cu, 11 Ag, 3 Au, 0.7 Se, 4 Te, 28 Pb.

The doré furnace is an oil-fired reverberatory, with a removable hearth 4 feet 1½ inches by 4 feet 0 inches, built of magnesite brick. The exit gases from the doré furnace pass under a waste-heat boiler, to a water scrubber for humidification, and then to the Cottrell. The scrubber and Cottrell solution is withdrawn for recovery of selenium. The residue collected in the scrubber and Cottrell is filtered, bagged, and returned to the roasting furnace.

Leached slimes are charged to the doré furnace with soda ash, silica, and niter. When the charge has melted, coarse charcoal is used to reduce metal from the slag, which is then skimmed. Charges are made until sufficient bullion has accumulated for refining. The doré slag is returned to the copper smelter.

The selenium matte, which forms a layer above the bullion, is decomposed by rabbling with soda ash and niter, the resulting soda-niter slag being treated for recovery of selenium and tellurium.

Air is blown onto the surface of the bullion, which is then cleared by thickening with ashes and skimming. The skimmings, known as selenium matte, are recharged to the doré furnace in the subsequent campaign. This process is repeated and finally the bullion is refined with niter until the fineness is about 980, and is then cast into anodes for parting in Balbach-Thum type cells of glazed porcelain.

Norddeutsche Affinerie, Hamburg, Germany. Norddeutsche's selection of the slimes-treatment flow sheet is predicated on the proximity of the Norddeutsche Affinerie's own lead refinery. It is interesting to note that the Norddeutsche process is somewhat similar to that used by the American Smelting & Refining Co., Barber, New Jersey, whose copper refinery is also close to a lead smelter.

The thickened slimes from electrolytic cells are pumped into a brick-lined oxidizer to which water and sulfuric acid are added to obtain 120 grams H_2SO_4 per liter. The mixture is heated to 60°C (140°F) with

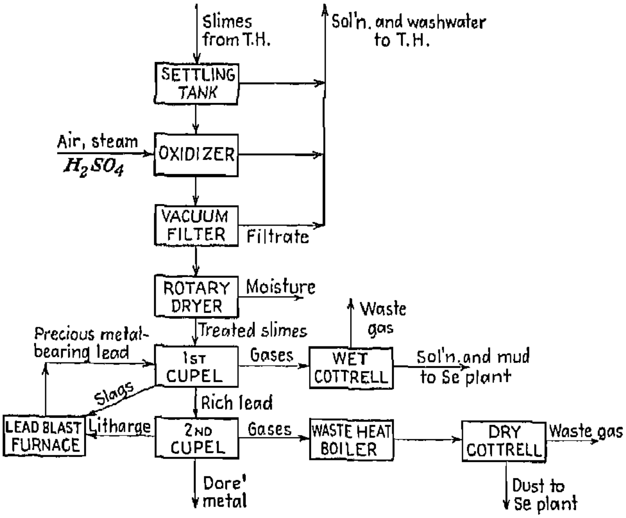

FIGURE 11-5. Norddeutsche Affinerie silver refinery flow sheet.[7] (*Courtesy of the American Institute of Mining and Metallurgical Engineers.*)

direct steam. Compressed air is blown through the tank to oxidize and dissolve the copper. Blowing is continued until the free acid content of the liquor becomes constant. The slimes are then settled and the clear liquor is returned to the tank house.

After leaching, the slimes contain only 2 to 3 per cent copper, compared to 16 to 20 per cent before treatment. The treated slimes are passed to a rotary vacuum filter and are dried on a drum dryer to 10 per cent moisture. These slimes are fed to the cupellation plant and contain 2 to 3 per cent Cu, 4 to 10 Se, 1 Te, 9 to 18 Pb, and 2 to 3 per cent silver plus gold. The slimes are processed with foreign slimes and with lead from the lead refinery containing 4.5 per cent silver plus gold. About 880 pounds of lead is required per ton of dry treated slimes. The charge is oxidized by blowing with air, and produces 660 pounds of rich lead and 2,000 pounds of slag per ton of treated slimes. The rich lead produced in the first cupel contains 30 to 40 per cent copper and is charged to the second cupel.

The products of the second cupel are silver bullion containing 99 per cent silver plus gold, and litharge containing 62 per cent lead, 13 per cent copper, and 4 per cent silver plus gold. The second cupel furnace can treat up to 10 tons of silver bullion per charge. The second cupellation requires 25 furnace-hours per ton of bullion, and consumes 2.8 tons of coal per ton of silver bullion produced.

The gas from the second cupellation is treated in a dry Cottrell. As a rule, the Cottrell dust is smelted in the lead blast furnace; when rich in selenium it is treated together with the mud from the wet Cottrell for selenium recovery.

The bullion from the second cupel is cast into anodes measuring 10 by 8 by ¾ inch and weighing 320 to 350 ounces. These anodes are electrolyzed in earthenware Moebius cells.

Outokumpu Oy, Pori, Finland. The anodes refined at Outokumpu have a very high nickel content (0.7 per cent), so that the resulting raw slimes require an intensive treatment to remove nickel and copper prior to doré furnace smelting.

Raw slimes are thickened, filter-pressed, and washed free of electrolyte. They analyze 11 per cent Cu, 45 Ni, 9 Ag, 0.5 Au, and 4 per cent Se. The washed raw slimes are air-roasted in a stainless steel electrically heated rotating drum, 2 feet 8 inches in diameter by 9 feet 10 inches long. Electrically heated air is circulated through the drum. The drum rotates at ¼ rpm and is maintained at a temperature of 350°C (660°F). The roasted slimes are milled to break up lumps, and are then digested with sulfuric acid. The digesting is done in two electrically heated cast-iron troughs below the sublimation temperature of selenium dioxide. The

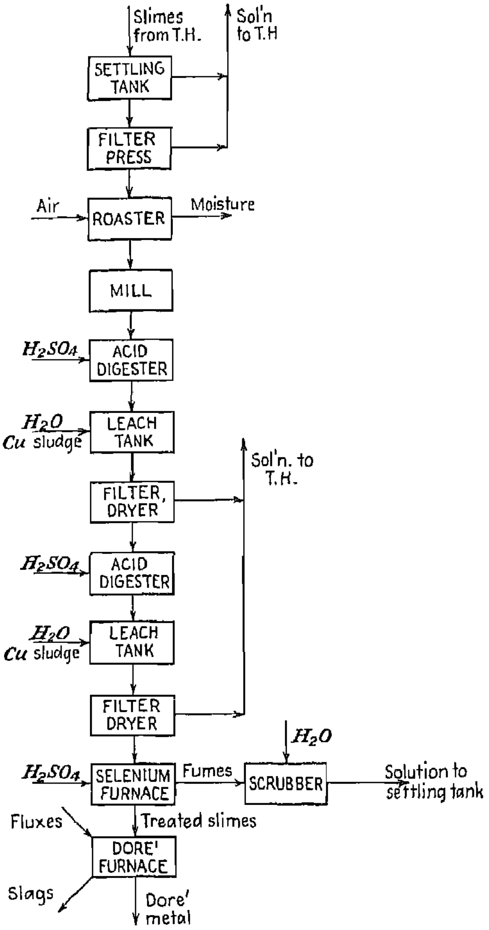

FIGURE 11-6. Outokumpu Oy silver refinery flow sheet.[7] (*Courtesy of the American Institute of Mining and Metallurgical Engineers.*)

digestion is done in batches, slimes being added gradually to the bath of hot concentrated acid. The acid consumption is 1.2 pounds per pound of slimes. The nickel oxide and the copper are sulfated on digestion. Some silver sulfate and selenium dioxide are also formed.

The digested slimes are water-leached to dissolve most of the nickel and copper and a part of the silver and selenium. The liquor is cemented on copper sludge to precipitate silver and selenium, then filter-pressed and returned to the tank house. The filtered slimes are called No. 1 leached slimes and contain about 6 per cent Cu, 12 Ni, 27 Ag, and 11 per cent Se. These slimes are dried, digested, and leached for a second time to remove almost all the remaining nickel and copper. The liquor is treated as for the first leach above. The No. 2 leached slimes contain 0.5 per cent Cu, 0.9 Ni, 36 Ag, and 13 per cent Se.

The No. 2 leached slimes are filtered and charged into cast-iron pans with a measured amount of concentrated sulfuric acid. The pans are then placed in an electrically heated stainless steel muffle furnace.

The roasting operation is a batch process and produces treated slimes containing less than 1 per cent selenium. The selenium dioxide and sulfur dioxide are drawn from the furnace by suction and are absorbed in weak sulfuric acid solution, forming selenium and additional sulfuric acid. The solution from the absorption towers is treated for selenium recovery.

The refined slimes and suitable fluxes are charged to a small oil-fired furnace. Smelting operations are simple due to the prior removal of copper, nickel, and selenium. The doré slags are charged to the copper anode furnace.

The doré anodes contain:

	Per Cent		Per Cent
Cu	1.12	Pt	0.02
Ag	92.69	Pd	0.05
Au	4.92	Bi	0.01
Se	0.03	Pb	0.006

These anodes are electrolyzed in Moebius cells.

Parting Plant Practice

Doré metal is parted electrolytically in either Balbach-Thum or the more generally used Moebius cells. Comparative operating data are given in Table 11-4.

At Canadian Copper Refiners Ltd., the Moebius cells are arranged in three groups of five cells each. Fifteen anodes are suspended in each cell, so that the total loading for fifteen cells is 34,000 troy ounces. Each set of three anodes is enclosed in a duck filter bag. On parting, the silver dissolves in the electrolyte at the anode and plates out as a nonadherent deposit on the cathode. The gold from the anode is collected as an insoluble mud inside the bag.

A wooden-frame basket with a filter-cloth bottom is suspended in each Moebius cell. Continually reciprocating wooden scrapers brush the silver crystals from the cathodes into the basket filter bottoms. The baskets are raised from the cells every 12 hours for removal of the silver crystals, which are washed with water in a filter-bottom stainless steel cart to remove all traces of electrolyte. The washed silver sand is dried and melted in a silicon carbide retort, 15,000 ounces at a time. Silver bullion is cast in 1,000-ounce bars, assaying 999.8+ fine Ag, 2 parts per million Au, 2 parts per million Se, and less than 1 part per million Pd.

TABLE 11-4. COMPARATIVE OPERATING DATA FOR MOEBIUS AND BALBACH-THUM CELLS[7]

Refinery	C. C. R.	E. R. & S.
Type of Cell	Moebius	Balbach-Thum
Electrolyte		
Ag, g/liter	100	90-120
Cu, g/liter	15	60 max.
Free HNO_3, g/liter	2	3-10
Circulation	Stirring by mechanical scraper	None
Current		
Current per cell, amp.	500	200
Current density, amp. per sq ft	30 cathode 44 anode	40 anode
Voltage per cell, volts	2.8	5.0
Current efficiency, per cent	93.5	
Kw-hr per troy pound Ag	0.276	
Anodes		
Composition, parts per thousand	905 Ag, 85 Au, 5 Cu	778 Ag, 193 Au
Size	9 by 6 by ½ inches	10¼ by 7½ by ¼ inches
Weight, troy ounces	150	70
Number per cell	15	10
Life	28-34 hours	2-3 days
Method of support	By clip from bus bar	In a cradle
Anode enclosure, form	Bag	Cradle, 2 per cell
Anode enclosure, size	21¼ by 2 by 15¾ inches	26 by 9¼ by 7¼ inches
Anode scrap, per cent	25	
Cathodes		
Number per cell	6	4
Material	Rolled silver sheets	Carbon strips
Size	20 by 12 by 1/16 inches	24 by 5 by ½ inches
Cells		
Material of construction	Steel, rubber-and-brick lined	Glazed earthenware
Number	15	20
Size	30⅞ by 30⅞ by 24 9/16 inches	49 by 24 by 9¼ inches
Cell arrangement	3 sets of 5 in series	20 in series
Hours before silver is removed	12	

Anodes are removed from the Moebius cell bags after 24 to 28 hours, scraped to remove the passive gold film, and replaced in cells for an additional 4 to 6 hours. When necessary, anodes ready to be scrapped are replaced in cells by new ones. Once every four days all anodes are removed. The bags are drained and emptied. The anode scrap after scraping is remelted in a graphite crucible and cast into doré anodes for parting.

The gold mud scraped from the anodes is combined with that from the bags, washed with water, and boiled with concentrated sulfuric acid to remove silver and selenium. The acid-leached gold is washed with water and drained on Filtros blocks. The gold sand is melted in a crucible furnace and cast into bars assaying 998+ fine Au.

At Electrolytic Refining & Smelting Co., in each Balbach-Thum cell, two acid-proof painted wooden cradles are immersed 1½ inches in the electrolyte. The cradle bottoms are covered with 12-ounce duck and five anodes are placed in each cradle, contact being made with a silver stud. The anodes in the two cradles in each cell are in parallel, while the cells are in series circuit.

The cell bottom is covered with carbon strips which serve as the cathode. Silver crystals are removed from the cathode by raking them up the sloping bottom. After the electrolyte on the silver has drained back to the cell, the crystals are washed as described above.

The mud is cleaned from the cradles daily after the first two days of each campaign, washed with water, and leached with sulfuric acid. Since the leached gold contains sufficient platinum, it is melted in a graphite crucible and cast into anodes for refining in Wohlwill cells.

Details of the cells used at Electrolytic Refining and Smelting Co. are given in Table 11-5.

On electrolysis gold is dissolved from the impure anode and deposited on the pure gold cathode. A.C. is superimposed on D.C. to flake the silver chloride off the anodes, which would otherwise tend to become passive. The silver chloride collects with some gold as a sludge at the bottom of the cell. This is used for making up electrolyte by dissolving in aqua regia, boiling off the nitric acid, and filtering. The filtration removes silver chloride and other impurities, which are melted to Wohlwill residue bullion and retreated in the doré furnace.

Palladium and platinum dissolve in the electrolyte. Periodically a portion of the electrolyte is withdrawn for recovery of the platinum-group metals and is replaced with fresh gold chloride solution.

As each cathode attains sufficient weight, it is removed, washed in cold water, and drained. The cathodes are melted and cast into bars which assay 999.7 Au, 0.2 Ag fineness. The anode scrap from the Wohlwill cells is remelted daily and cast into new anodes.

Scrap from both Balbach-Thum and Wohlwill cells is worked up in a diminishing number of cells until the particular batch or campaign is worked out almost completely. The final scrap is then insufficient to run one cell.

TABLE 11-5. DETAILS OF WOHLWILL CELLS[7]

Type of Cell	Wohlwill
Electrolyte	
Au	70-90 g/liter
HCl	150 g/liter
Temperature	65°C (150°F)
Circulation	By glass propeller
Current	
D.C. per cell	90-95 amperes
Current density	50 amp per sq ft
A.C. per cell	105 amp
Voltage per cell	1.5 volts
Anodes	
Composition	996 Au, 1.5 Ag, 0.5 Pt, 1.0 Pd, parts per thousand
Size	6 by 2¾ by ¼ inches
Weight	35 oz each, 315 oz per cell
Number per cell	9
Per cent scrap	25
Cathodes	
Material	Pure gold
Size	11 by 2¼ by .015 inches
Number per cell	11
Cells	
Material	Glazed earthenware
Number of cells	4
Volume per cell	20 liters
Heating	Electrically heated water jackets

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* Deceased.

Copper Works, Perth Amboy, N. J.; W. C. Smith, Cerro de Pasco Copper Corporation, New York, N. Y.; R. H. Waddington, The International Nickel Co. of Canada, Ltd., Copper Cliff, Ont.; S. Wallden, Bolidens Gruvaktiebolag, Rönnskar, Sweden; F. S. Weimer, Anaconda Copper Mining Co., Great Falls, Montana.

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5. International Nickel Co. issue, *Can. Mining J.*, **67**, 454-5 (1946). Slimes acid-roasted, acid-leached, and smelted.
6. Mosher, M. A., "Recovery of Precious and Secondary Metals from Electrolytic Copper Refining," *Trans. Am. Inst. Mining Met. Engrs.*, **106**, 427-40 (1933). Detailed description of practice at the Raritan Copper Works; oxidizing roast, acid leach, smelting, etc.
7. Schloen, J. H., and Elkin, E. M., "Treatment of Electrolytic Copper Refinery Slimes," *J. Metals*, May, 1950; *Trans. Am. Inst. Mining Met. Engrs.*, **188**, 764-77 (1950). The greater part of the material in the present chapter appeared in this publication.

Patents

8. Betterton, J. O., and Lebedeff, Y. E., U. S. Patent 2,378,824, June 19, 1945. Process for recovering selenium. Selenium-bearing materials mixed with alkali metal salt (Na_2CO_3, NaCl, $NaNO_3$, or a mixture of these), heated at 800 to 850°C (1470 to 1560°F) for 2 to 3 hours, and water-leached.
9. Bolidens Gruvaktiebolaget, Brit. Patent 440,004, Dec. 18, 1935. An improved method of refining selenium. Slimes fused with caustic soda and carbon at 400°C (750°F), and water-leach liquor blown with air to precipitate gray selenium.
10. Clark, C. W., U. S. Patent 2,322,348, June 22, 1943. Process for recovering selenium as selenium dioxide from copper refinery slimes. Slimes digested with sulfuric acid and roasted at 480°C (900°F).
11. Keller, E., U. S. Patent 1,110,493, Sept. 15, 1914. Process for treating anode residues. Slimes baked with sulfuric acid at 230°C (450°F), then water-leached.
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Chapter 12

The Fire Refining of Copper

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At the present time there are two different categories of fire-refining processes performed on copper.* These are:

(*a*) The refining of selected qualities of blister copper to give fire-refined tough-pitch high-conductivity copper.

(*b*) The refining of blister copper to give tough-pitch copper of normal commercial purity.

In addition to these, the usual fuel-fired furnace process involved in melting of electrolytic cathodes to give tough-pitch high-conductivity copper is often regarded as a refining process because the copper during melting absorbs oxygen and sulfur which must be removed in the furnace before casting. Although the resulting product contains a slightly lower percentage of copper than the cathodes before melting, and the process is therefore not actually one of refining, the removal of sulfur and adjustment of the oxygen content requires steps very similar to those taken in "fire refining" in the stricter sense of that term. Because of this fact, much of the discussion in this article will be applicable to the process of cathode melting and casting as well as to categories (*a*) and (*b*) above.

In each case scrap material may be incorporated in the charges, and the types and amounts of such scrap which may be so employed depend on the impurities present; naturally there is more scrap in operations under (*b*), and indeed it is sometimes the practice to employ all-scrap charges.

While the refined products are normally restricted to those listed above, the adoption of modified procedures leads to the production of special qualities, as for instance tough-pitch silver-bearing high-conductivity copper, phosphorus-deoxidized copper, and many others, these all being conveniently produced with only slight changes in procedure.

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* The discussion in this chapter refers to the furnace refining of copper for direct marketing, not to the partial furnace refining of blister copper for production of anodes.

It will be appreciated from the above that fire refining has a wide scope, and, while the process is a versatile one, the practice has become distinctly specialized at different plants, according to the raw materials employed and the products required. The scale on which operations are conducted, namely in quantities from 2 tons up to 400 tons per charge, is indicative of the variations which are currently in existence.

In regard to the refining operations as applied in primary metal production, it is necessary to consider the whole scheme of recovery of the metal from the particular ore bodies, because the compositional features of the latter, namely impurity and precious-metals contents, determine the practice which shall be followed. Fire refining provides only a limited scope for the elimination of impurities and it does not provide for the recovery of precious metals.

At the present time about 72 per cent of the world's production of primary copper is processed by electrolytic refining followed by melting of the cathodes in fuel-fired reverberatory furnaces, while only about 6 per cent is fire refined direct from blister to give high-conductivity copper (method *a* above) and 8 per cent is fire refined into copper for other than high-conductivity purposes (method *b* above). The balance of 14 per cent is marketed in the form of copper cathodes or as shapes which are produced by special methods other than fire refining, *e.g.*, the electric melting of cathodes. The latter practice has made rapid progress, but, while still further progress in electric melting can be anticipated, it is generally considered that electrolytic and fire refining will continue to be the predominant production methods for many years.

Types of Refining Furnaces

Refining furnaces are mostly of the reverberatory type, and have been developed from the small furnaces which were used in the original Welsh process for the smelting and refining of copper. Whereas the capacity of the original coal-fired furnaces was limited to less than about 20 tons, rapid developments followed the introduction of gas and fuel oil for firing purposes, and furnace sizes were enormously increased in the period 1890-1910. Fuel oil, gas, or pulverized coal—depending on availability and price—is now used almost universally, and the capacities of modern reverberatory refining furnaces are usually of the order of 150 to 400 tons for the casting of wirebars and 40 to 100 tons for the casting of shapes. The development of large furnaces led to the introduction of mechanical casting methods for wirebars, the conservation of heat by means of waste-heat boilers, and many other improvements in furnace design and operation.

The larger furnaces are naturally installed only by the larger primary copper producers and custom refiners, and for smaller concerns it has been necessary to adhere to small melting units. It is believed that 200-ton capacity furnaces are the largest which are currently used for fire refining blister copper direct.

A notable development of the last 25 years, particularly in Europe, has been the adoption of rotary melting furnaces of capacities from about 2 tons up to 20 tons, though larger units have been installed in some instances. The principal advantage of rotary designs is the considerable reduction of time necessary for completion of the cycle of operations, this being from about one-eighth to one-third of that necessary in the case of reverberatory practice. It is to be noted, however, that the rotary furnace has not entirely supplanted the small reverberatory furnace, and probably on the whole there is little difference in operating costs and efficiency. Both the small reverberatory and rotary furnaces are of particular advantage for the casting of special shapes, which may range from the usual sizes of billets and cakes to the very large castings for fabrication into heavy sheet for locomotive fireboxes and chemical vessels.

The choice of refractories for refining furnaces is a matter on which many different views are held; this is partly because of widely differing experience according to the particular grade of copper being refined, the more impure varieties being especially severe on refractories. In the recent construction of a 400-ton furnace at El Paso for melting of cathodes, the hearth is of silica brick, with magnesite brick side walls below the metal line, silica brick in the main roof, and magnesite-chrome brick in the verb arch and supporting arch for uptake. In some furnaces for the refining of blister copper direct there is a more extensive use of magnesite and chrome-magnesite bricks. The idea of having a suspended roof, which is a feature of smelting practice, has not yet been adopted in refining furnaces to any great extent, though a few furnaces have already been built with this method of construction.

The Refining Process

Essentially in its simplest form the fire-refining process comprises five distinct phases, these being in sequence:

(1)	Charging	1 to 3 hours
(2)	Melting	8 to 11 hours
(3)	Oxidizing (flapping) and skimming	3 to 5 hours

(4)	Poling	2 to 3 hours
(5)	Casting	4 to 9 hours

The times quoted are those usual for reverberatory practice, and are varied so as to operate on a 24-hour cycle for each charge. Sometimes a good time margin is obtained, though in many cases it is difficult to complete in the 24-hour cycle, and some of the recent suggestions, such as oxygen enrichment of air for blowing and preheating of air for combustion, have been made with the main idea of assisting the time cycle. In the case of rotary-furnace refining, the complete cycle of operations is performed usually in from 3 to 12 hours, permitting two to eight casts per day, the shorter time being sufficient with the smaller rotary furnaces of about two tons capacity.

In essence, the refining process consists of oxidation in order to cause the impurities to pass into slags or be removed by volatilization, followed subsequently by elimination of the excess oxygen and at the same time control of the gas contents.

The charging and melting stages do not call for comment, as these are quite straight forward and merely involve lengthy time cycles for scrap charging, blister charging, sealing of doors, top charging, resealing doors, and complete melting, in the order given.

In the oxidation stage which follows, the processes of flapping (exposing the surface of the molten metal by a surface skimming action) and blowing (with air admitted through iron pipes) are continued until the oxygen content of the metal is about 0.6 to 0.9 per cent; the upper figure must be achieved when the charge is even slightly impure and high-conductivity wirebars are to be cast, but the lower figure suffices for the refining of high-purity cathodes and also blister and low-grade charges when ingots or ingot bars are the products. During the oxidation stage slags are removed as necessary, these naturally containing large quantities of copper as well as the iron and other impurities, and in consequence they are reserved for smelting.

After completion of all slagging operations the poling stage is commenced. This is accomplished by covering the bath of metal with coal or coke and thrusting green timber (hard wood) below the surface of the metal, an operation that gives a vigorous evolution of reducing gases, which combine with the oxygen contained in the metal. Owing to the fact that such gases, particularly hydrogen, are soluble in copper, the process of poling must be carefully controlled. The question of gas content of the refined metal is discussed in further detail later, because of its fundamental importance in copper refining.

From the practical aspect the poling operation must be carried to the point which gives level-set surfaces on the particular cast products which are being produced. Thus the poling process, as a separate stage, is very much integrated with the casting stage. The tough-pitch condition is normally obtained with oxygen contents ranging between 0.025 and 0.05 per cent in the case of fairly high-purity material, but with very low-purity copper the oxygen content is required to be of a higher order.

The casting stage calls for great skill and control. Actually the particular size and shape of the cast product determines the degree to which the poling must be taken, partly because of the fact that oxygen pickup during casting is variable, and this naturally affects the "set"; in this matter mold temperature also has an influence. In practice, shapes which are relatively shallow can be cast with an initially higher oxygen content than shapes which are relatively deep, though it is not possible to lay down definite rules about the relationship existing between mold shapes, purity of metal, temperature, and oxygen content.

One further point is that correctly poled metal must be cast within a certain time limit, otherwise it will go off set, due to the pickup of sulfur rather than to a change in the hydrogen and oxygen balance, as was at one time held to be the explanation.

It will be interpreted from the foregoing remarks that the fire refining of copper to give tough-pitch products is a metallurgical operation which is controlled more by practical observations than by laboratory control. This is to a large extent true, but there is no doubt that the present knowledge on gaseous reactions has assisted enormously in a full appreciation of the points which were hitherto observed by practical refiners.

Layout and Equipment

While considerable latitude is sometimes exercised in the layout of refineries, particularly in the small ones casting special shapes, all of the modern plants for wirebar casting follow the general pattern of arrangement in five bays, these being (1) the raw materials bay (often not roofed); (2) the charging bay; (3) the furnace bay; (4) the casting bay; and (5) the inspection and dispatch bay.

Each of these bays has a width of about 60 ft with the exception of the furnace bay, which has a width of only about 20 ft. The main bays are equipped with cranes and other mechanical handling facilities, including charging machines in the charging bay, and a conveyor between the casting bay and the inspection bay to convey cast products from the water bosh of the casting wheel onto the inspection conveyors.

Space limitations render it impossible to detail either the casting equipment or the general mechanical handling arrangements, though an appreciation of the former is possible from Figure 12-1. The casting wheels are of the Walker or Clark pattern, 25 to 40 ft in diameter, with multi-pocket molds (3 to 5 pockets per mold) for wirebar casting, and with these a casting rate up to 70 tons per hour may be attained. Ladle design differs slightly for the Clark and Walker methods, and an important point is that the mounting must be such that a minimum drop of molten metal occurs when casting into the molds passing beneath the ladle lips.

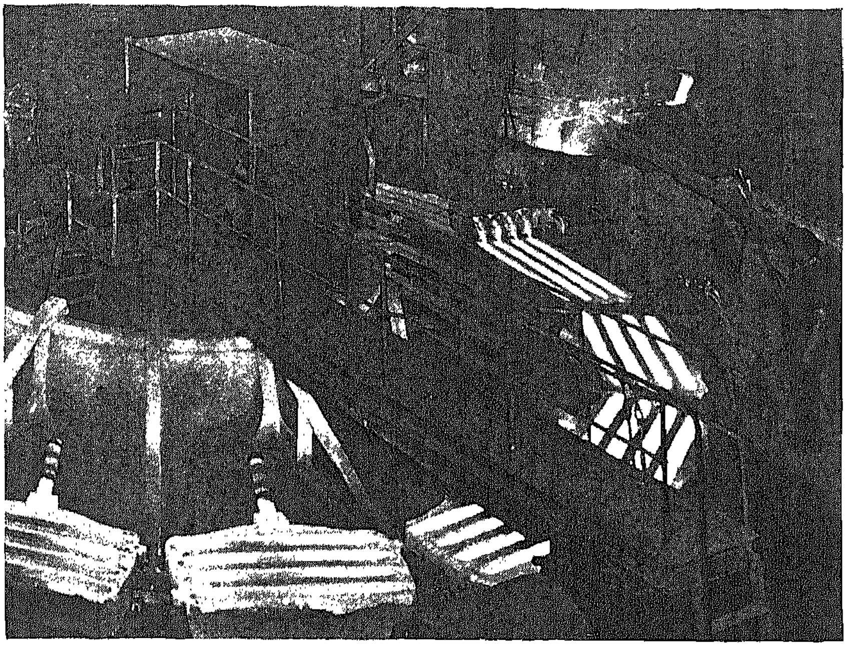

FIGURE 12-1. Casting wirebars into four-bar molds on Walker casting wheel. (*Courtesy of British Copper Refiners, Ltd.*)

For wirebar casting, solid copper molds are invariably employed, and it is the universal practice for these to be dressed with bone ash, applied as a wash from a spray gun. Great importance is attached to the grade of bone ash, the composition and fineness having an influence on the smoothness of the resultant cast products. To attain a satisfactory life from the molds, the casting temperature must be controlled at approximately 1105 to 1115°C. Peening of the mold pockets between casts prolongs their life, but even with the utmost precautions, the life is relatively short, say 8 to 25 days, so that the cost of molds is a considerable item.

Where large tonnages of cakes or billets of regular size are required, these may be cast direct from reverberatory furnaces, though this practice is rather unusual, as the requirements seldom justify this method.

Instead, it is more usual to adopt a "side casting" technique, involving the use of ladles or holding furnaces of about 5 tons capacity, which receive the metal from the main furnace, and are transported to a convenient position for adjustment of temperature and pitch, followed by deoxidation if necessary and then by casting. The latter is quite frequently performed with a small wheel, say of 10 ft. diameter approximately, such as is illustrated in Figure 12-2, which shows an arrangement for the casting of small billets in water-cooled molds.

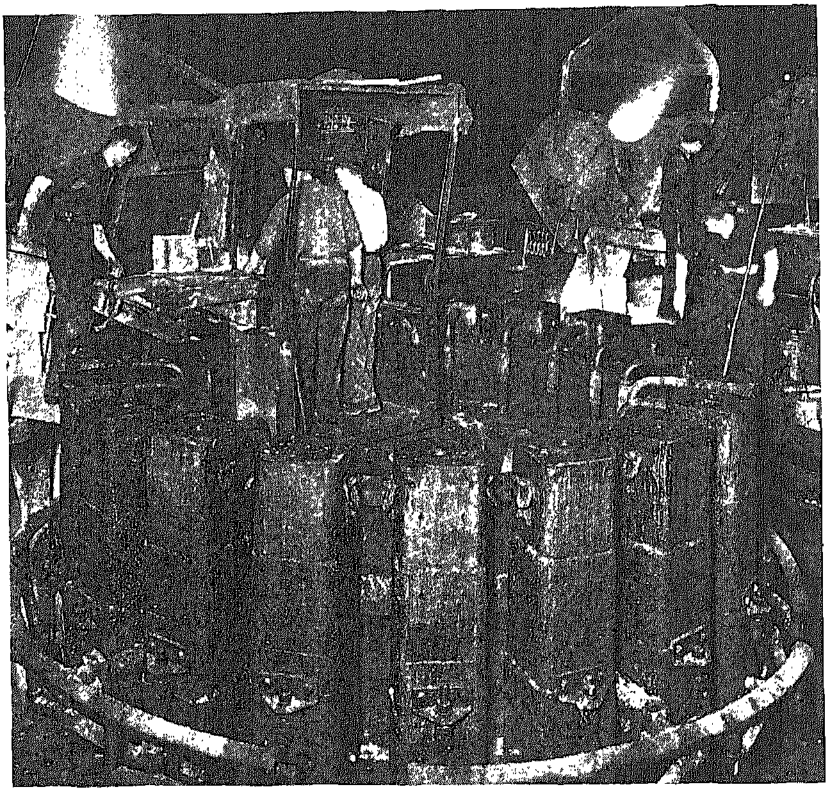

FIGURE 12-2. Casting small-diameter billets from a 5-ton portable holding furnace. (*Courtesy of British Copper Refiners, Ltd.*)

For the casting of shapes, while the molds are often of solid copper, more generally water-cooled molds are used, these being either of the type introduced by the American Metal Company, and made by drilling solid copper shapes so as to form water passages, or of a built-up type more resembling the original Junker mold, in which the face of the mold is either a wrought copper or steel tube. These water-cooled types have been of great benefit in meeting the demands for shapes, both of the deoxidized and oxygen-free varieties of copper as well as the tough-pitch types.

For tough-pitch copper hot water is circulated through the molds, which are dressed with bone ash, while for deoxidized metal the water is cold and oil-base mold dressings, such as graphite and mineral oil, are used. *With the latter it is also customary to admit a slight stream of* water into the mold pockets during casting, with the object of floating carbonaceous residues away from the mold walls and so giving better surfaces on the cast products.

Removal of Impurities in Fire Refining

While a few elements are removed by volatilization and pass away in the furnace gases (including sulfur, cadmium, and zinc), the removal of impurities is essentially a matter of oxidation and slagging, and as such is naturally related to the heats of formation of the metallic oxides, and also to the solubility of the oxides in copper.

Magnesium, aluminum, and iron are readily removed, passing into slags as silicates. Nickel is a persistent impurity, probably because its oxide is soluble in copper, though the heat of formation of the oxide is high. Tin can be almost wholly eliminated in a basic slag, and lead removal is favored by an acid slag, though this element is a much more persistent one and indeed its removal is considered to entail too much expense to be economic.

Arsenic and antimony are not appreciably reduced under normal refining conditions; but if, after completion of normal slagging, additions of soda ash and lime are made to the charge, arsenic and antimony may be slagged away, and with successive treatments almost complete removal of these elements may be achieved[2, 3].

Removal of selenium and tellurium has been accomplished by a soda ash-lime-coal flux mixture, but as this requires reducing conditions, and a complete removal of the slag afterwards, the method has not been adopted commercially[4, 5].

Bismuth is a persistent impurity and means for its elimination during fire refining are not known.

Apart from the references mentioned, few systematic data on removal of impurities have appeared since the work of Wanjukoff[6] and Stahl[7] about 40 years ago.

Gas Reactions in Refining

As already pointed out, the attainment of the tough-pitch condition is bound up with gas solubilities and reactions, but only within the last

25 years have definite systematic studies been made of the subject. The elements playing a part in the process are oxygen, hydrogen, sulfur, and carbon.

It has long been known that the solubility of hydrogen increases with temperature in both the solid and liquid conditions, and there is a sharp change at the melting point. Allen and Hewitt[8, 9] showed that the solubility of hydrogen in molten copper varies greatly with the amount of oxygen present, being much higher in metal having a low oxygen content; they also showed that the evolution of the excess hydrogen at the solidification point and its reaction with part of the oxygen present to form steam, which is insoluble and thereby gives a great expansion effect to the solidifying metal, is the fundamental reaction in the production of tough-pitch metal. Thus a balance of hydrogen and oxygen contents was considered to be the important requirement, and when this was out of balance, the metal was either underpoled or overpoled. The amount of hydrogen required for the reaction is extremely small, so much so that this can always be derived from the moisture in the furnace atmosphere.

While the oxygen-hydrogen reaction is the main one, much suspicion has always been attached by practical refiners to sulfur, especially as this can be picked up at a late stage from the furnace gases while the refined metal is held for casting. Thus a subsidiary reaction occurs between minute amounts of sulfur and oxygen, upsetting the pitch. The influence of sulfur[10, 11], and of carbon[11, 12] have recently been investigated and confirmation obtained of the sulfur-oxygen reaction. Carbon is of importance under certain conditions only.

A review of the part which gases play in the refining of copper has recently been given by Phillips[13].

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Chapter 13

The Hydrometallurgy of Copper

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The hydrometallurgy of copper is concerned with those processes and methods whereby dissolution of copper values from copper-bearing materials is effected through the use of an aqueous solvent. The subsequent recovery of metallic copper or an enriched copper compound is effected after separation of the copper-bearing solution from other residual matter through either chemical or electrolytic precipitation. The processes have been limited largely to copper-bearing materials that because of grade or composition do not lend themselves to economic methods of concentration and pyrometallurgical extraction.

In general, then, hydrometallurgical methods would apply more often to those groups of copper-bearing materials classed as the low-grade native coppers, the oxidized, or the mixed oxide-sulfide minerals. These materials, as a whole, do not lend themselves to other methods of concentration, either because treatment costs are too high or because the over-all recovery of the contained copper is too low. Recent trends point to a combination of hydrometallurgical methods for the recovery of the oxide minerals, coupled with flotation methods for the recovery of the sulfide portion[1].

Leaching is neither new nor unusual. Recorded evidence indicates that copper was extracted by hydrometallurgical methods on a small scale in Hungary in the fifteenth century[2]. Copper has been recovered by wet methods to some extent from that time to the present.

The basic chemistry involved in the dissolution of the copper is not complex, nor is the subsequent precipitation of the copper from the aqueous solutions. The lack of widespread application of the methods, then, is not due to complexity of metallurgical problems but rather to the complex materials-handling problems resulting from the large volumes of solutions and the large tonnages of low-grade, copper-bearing materials involved.

No satisfactory solvent has been found for the recovery of copper and precious-metal values in a single leaching cycle. It is quite conceivable that if the precious-metal values were high enough, a process might be developed for a double leach, in which the copper values were first extracted with a suitable solvent, followed by a leach for the extraction of the gold and silver. The complexity and cost of such a process have in general resulted in the adoption of pyrometallurgical methods where precious values have been high enough to warrant recovery.

The search for possible solvents for copper-bearing materials, essentially the copper minerals, resolves itself into those that have selective action for the contained copper while having limited action on the gangue minerals associated with the copper values. In general, the gangue minerals are either siliceous or less commonly a gangue of dolomite or limestone. A dolomite or limestone gangue would immediately eliminate acid solvents as they could not have selective action on the contained copper.

In addition to selective action, the solvent must either be cheap, or regenerative to such an extent in the process of precipitation of the copper from solution that the net consumption of solvent per pound of recovered copper is low enough to justify the use of a more expensive solvent. Solvents meeting this requirement must also be effective in cold, dilute concentrations. It is evident that dealing with large tonnages of low-grade materials, as they do, hydrometallurgical processes could not compete if it were necessary to leach at elevated temperatures. In some instances due to severe climatic conditions in winter months, it has been found economical to heat solvents to a limited extent to improve over-all recovery[3].

Higher concentrations, while more effective than more dilute solutions, pose problems in that they are also more active in attacking the gangue minerals associated with the copper minerals. In addition, severe corrosion problems usually arise in the maintenance of handling equipment.

Thus hydro-dissolution does not take advantage of two basic principles for speeding up chemical reactions, namely, those concerned with temperature and effective concentration. To insure maximum economic recovery, leaching time then becomes the limiting factor. Increased time for increased recovery has the adverse effect of requiring more inventory tie-up of both solvent and mineral, as well as a larger investment in capital equipment per unit of copper recovered.

Although extensive experimental work has been done with various solvents, as evidenced by numerous patents and proposed methods for recovering copper by hydrometallurgical methods, only three solvents have found appreciable commercial application: sulfuric acid, sulfuric acid-ferric sulfate, and ammoniacal ammonium carbonate. Hydrochloric acid, sulfurous acid, ferrous chloride, ferric chloride, cupric chloride, and nitric acid or various combinations of these and the above have been suggested as offering commercial potential, but their use has been limited largely to pilot-plant and laboratory activity[4]. They are designed primarily for the dissolution of precious metals as well as the copper. It is not to be inferred that one or more of these solvents may not become economically feasible but rather that in their present state of development they are not in a competitive position with the more widely used solvents as noted.

Other processes involving roasting previous to the leaching, in which the slightly soluble copper sulfide minerals would be converted to their oxides, have been suggested from time to time[5]. In general, roasting is much too expensive a unit operation to be carried out on a large scale on low-grade copper ores.

Some experimental work has been carried out on the possible treatment of roasted copper concentrates[6]. While this is promising, the problem of precious-metal recovery is still at issue. With further improvement in methods of copper concentration, it is probable that the residue containing the undissolved precious metals can also be upgraded to the extent of warranting separate treatment for their recovery. Such costly unit operations as reverberatory smelting and converting would be eliminated. Power costs *vs.* fuel costs would be an important consideration, as will be evident in the discussion of methods of precipitation of copper from solution. In pyrometallurgical treatment, concentrates of highest grade are not necessarily the cheapest to process, because of the requirement of sufficient sulfur in the matte to furnish the necessary fuel for the converting step.

Chemistry of Dissolution

The chemistry involved in the dissolution of copper minerals is essentially simple decomposition in the case of the oxidized minerals, and oxidation-reduction reactions in the case of the sulfide minerals. The products of the reaction are water-soluble or soluble in excess solvent. The base-metal sulfides are generally insoluble in acids or bases and require strong oxidizing agents for their decomposition.

The various oxides, silicates, carbonates, and sulfides in the associated gangue may undergo similar reactions to form soluble salts. The amount of these dissolved impurities depends largely on the nature of the gangue, and may result in the excessive consumption of solvent, as well as foul the resultant copper-bearing solution. Inasmuch as each individual ore offers its own problems as to composition, it is difficult to generalize upon the adaptability of a specific solvent to meet the variety of conditions of association that might be present.

The dissociation and dissolution of most of the pure copper minerals have been studied[7], out of which research has evolved valuable basic information that does offer a method of eliminating solvents that are not adaptable. Some of these minerals and their reactions will be discussed in further detail.

Native Copper

Ammoniacal ammonium carbonate is the principal solvent for native copper[8]. The copper undergoes a typical reaction in which "ic" salts oxidize metallic copper to form cuprous salts. The ammonium complex, cupric ammonium carbonate,* is actually the solvent, forming cuprous ammonium carbonate in the reaction with copper. To prevent hydrolysis of the complexes an excess of free ammonium is necessary, thus the reference to ammoniacal ammonium carbonate. The cuprous ammonium carbonate formed can be reoxidized to the "ic" form by passing air through the "ous" solution in the presence of ammonium carbonate to complete the reaction. The effective reagents are thus ammonium carbonate and oxygen, with cuprous ammonium carbonate an intermediate product and free ammonia a solvent to permit dissolution of the products of the reaction.

The reactions follow:

$$Cu + Cu(NH_3)_4CO_3 = Cu_2(NH_3)_4CO_3 \qquad (1)$$

$$2Cu_2(NH_3)_4CO_3 + 4(NH_4)_2CO_3 + O_2 = 4Cu(NH_3)_4CO_3 + 4H_2O + 2CO_2 \qquad (2)$$

The Calumet & Hecla company has successfully developed this method of dissolving copper to recover native copper from tailings too low in copper concentration to be effectively recovered by any other process[9].

Copper undergoes other similar oxidation-reduction reactions, which, while they have not found adaptation for leaching native copper, have found important application in the hydrometallurgical processing of other copper minerals.

Typical reactions, which will be discussed in greater detail as they apply to unit operations, follow:

$$Cu + CuCl_2 = 2CuCl \qquad (3)$$

$$Cu + Fe_2(SO_4)_3 = 2FeSO_4 + CuSO_4 \qquad (4)$$

$$Cu + CuSO_4 + FeCl_2 = 2CuCl + FeSO_4 \qquad (5)$$

---

* While this and other similar complexes are now referred to as the ammoniated copper salt, the older nomenclature will be used in this chapter.

Oxidized Copper Minerals

Azurite [$Cu_3(OH)_2(CO_3)_2$] and malachite [$Cu_2(OH)_2CO_3$] dissolve readily in dilute acids with the evolution of CO_2 in the decomposition of the carbonate, with no net loss of acid in the decomposition. They are also soluble in ammoniacal solutions, forming the complex cupric ammonium salt without intermediate oxidation, as is necessary in the dissolution of native copper. Ammonia is necessary not only to the reaction but also to prevent hydrolysis. Typical reactions follow:

$$Cu_3(OH)_2(CO_3)_2 + 3H_2SO_4 = 3CuSO_4 + 2CO_2 + 4H_2O \qquad (6)$$

$$Cu_3(OH)_2(CO_3)_2 + 10NH_4OH + (NH_4)_2CO_3 = 3Cu(NH_3)_4CO_3 + 12H_2O \qquad (7)$$

$$Cu_2(OH)_2CO_3 + 2H_2SO_4 = 2CuSO_4 + CO_2 + 3H_2O \qquad (8)$$

$$Cu_2(OH)_2CO_3 + 6NH_4OH + (NH_4)_2CO_3 = 2Cu(NH_3)CO_3 + 8H_2O \qquad (9)$$

Reactions 7 and 9 were basic reactions in the hydrometallurgical processing of ores by the Kennecott Copper Corporation at Kennecott, Alaska. The Kennecott ore was made up of both sulfides (essentially chalcocite and covellite) and carbonates (malachite and azurite) associated in a dolomite-limestone gangue. Because of the nature of the gangue minerals, acid leaching could not be utilized without excessive acid consumption.

The sulfide minerals were recovered by conventional concentration methods, and the tails containing about 1 per cent copper, mostly in the form of carbonates, were subjected to an ammoniacal leach. Recovery of the contained copper was about 80 per cent. The flow sheet used and other pertinent data concerning the operations have been described in the literature[10].

Tenorite. Tenorite (CuO), which dissolves readily in dilute acids, is also soluble to a more limited extent in ammoniacal solutions. Typical reactions follow:

$$CuO + H_2SO_4 = CuSO_4 + H_2O \qquad (10)$$

$$CuO + 2NH_4OH + 2(NH_4)_2CO_3 = Cu(NH_3)_4CO_3 + 3H_2O \qquad (11)$$

Cuprite. Cuprite (Cu_2O) is not as soluble in dilute acids as tenorite, and in the dissolution only one-half of the contained copper goes into solution, the balance remaining in the residue as elemental copper according to the following reaction:

$$Cu_2O + H_2SO_4 = Cu + CuSO_4 + H_2O \qquad (12)$$

An oxidizing agent such as ferric sulfate [$Fe_2(SO_4)_3$] is essential to complete the dissolution of the elemental copper, as noted in the reactions for native copper:

$$Cu + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4 \qquad (4)$$

The oxidation can also be effected by aeration, as the copper is in a finely divided state, but a more active oxidizing agent is much more effective.

In ore containing cuprite as a principal mineral, the combination of an acid and an active oxidizing agent is utilized for complete and rapid dissolution.

Chrysocolla. True chrysocolla [$CuSiO_3.2H_2O$] is readily soluble in dilute acids. However, the term chrysocolla is often used to include all copper silicates, many of them minor or complex silicates, which do not dissolve so readily. Dioptase ($CuSiO_3.H_2O$), for example, is acid-soluble but dissolves more slowly than true chrysocolla. Because of the difficulty of obtaining pure samples for study, the chemistry of the dissolution of many copper silicates has not been established. A typical reaction follows:

$$CuSiO_3.2H_2O + H_2SO_4 = CuSO_4 + SiO_2 + 3H_2O \qquad (13)$$

It will be noted that free silica is a product of the reaction. Since dilute acid concentrations are normally used for leaching, the SiO_2 often precipitates as a silica gel rather than as a granular product. As a result, many operating difficulties are encountered in the leaching, clarification, and washing when ores of this nature are treated by wet methods.

Brochantite. Brochantite [$Cu_4(OH)_6SO_4$] is a basic sulfate that is soluble in dilute sulfuric acid according to the following reaction:

$$Cu_4(OH)_6SO_4 + 3H_2SO_4 = 4CuSO_4 + 6H_2O \qquad (14)$$

It will be noted that in the dissolution four equivalents of $CuSO_4$ are formed for each three equivalents of sulfuric acid used. Thus, in a precipitation method which regenerates the solvent, sulfuric acid can be considered a product of the dissolution.

In the ore deposits at Chuquicamata, Chile, brochantite is one of the major minerals. The so-called "oxide" ore is a highly altered granite containing small veins of brochantite, with minor amounts of other oxide minerals. The ore has lent itself to hydrometallurgical processing with recoveries as high as 98 per cent on the oxide portion. In addition, for each pound of copper recovered from the ore, approximately 0.4 pound of sulfuric acid is generated. Consequently, without recourse to any other supply of acid this amount has been sufficient to take care of all losses of sulfuric acid inherent in the process.

Associated with the "oxide" ore are some sulfides, which are extracted with the use of ferric sulfate as a leaching agent. This solvent for sulfide minerals will be discussed in greater detail. The flow sheet and operating procedure used by the Chile Exploration Company at Chuquicamata have been covered in the literature[11].

Chalcanthite. Chalcanthite [$CuSO_4.5H_2O$] is a water-soluble copper mineral. It can be formed by natural oxidation, through the combined action of air, water, and iron salts on exposed copper sulfide minerals such as might remain in abandoned stopes or fractured areas. It can also be a product of mine fires, which sometimes occur in sulfide ores. This water-soluble copper accounts for most of the copper present in mine waters.

Natural oxidation of sulfide minerals has been utilized in commercial leaching operations. They will be discussed in greater detail.

Atacamite. Atacamite [$Cu_2Cl(OH)_3$] is a minor constituent of some oxidized copper minerals. It is acid-soluble; in the dissolution chloride ions are added to the solution. These ions can add to the problem of purification of resultant solutions before subsequent precipitation of the copper values. A typical reaction follows:

$$Cu_2Cl(OH)_3 + 2H_2SO_4 = 2CuSO_4 + HCl + 3H_2O \qquad (15)$$

Sulfide Minerals

Base-metal sulfides are insoluble in dilute acids and require the use of strong oxidizing agents for their decomposition. More powerful oxidizing acids such as concentrated nitric acid will decompose sulfides, but they do not find application as leaching agents. It has been suggested that nitric acid be used in conjunction with sulfuric acid for this purpose, in which case the NO_2 liberated in the decomposition of the nitric acid by sulfuric acid would serve as a strong oxidizing agent. Procedures of this nature have found application in laboratory methods for analytical purposes, but have not found favor in commercial dissolution. Obviously a leaching agent of this type would present serious handling problems.

Covellite. Covellite (CuS) will dissolve in ferric sulfate or ferric chloride solutions according to the following oxidation-reduction type of reaction:

$$CuS + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4 + S \qquad (16)$$

Elemental sulfur is a product of the reaction, which proceeds slowly at normal room temperatures. In ores that have lent themselves to hydrometallurgical processing, covellite has not been a predominant mineral.

Chalcocite. Chalcocite (Cu_2S) dissolves in two distinct and separate reactions, the first of which is fairly rapid, taking place according to the following reaction:

$$Cu_2S + Fe_2(SO_4)_3 = CuS + CuSO_4 + 2FeSO_4 \qquad (17)$$

The second involves the dissolution of the CuS formed in the first. This reaction is the same as given for the dissolution of covellite:

$$CuS + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4 + S \qquad (16)$$

It proceeds much less rapidly than the first reaction, but on the other hand much more rapidly than the dissolution of the pure mineral. Thus, while covellite does not lend itself to satisfactory extraction by leaching methods, ores containing chalcocite as the principal sulfide mineral have responded to this method of treatment. Bornite (Cu_5FeS_4) behaves in much the same manner as chalcocite.

It should be noted that a combination of air and sulfuric acid has little action on chalcocite and virtually none on covellite. Thus, it would appear that oxidation by natural processes of either chalcocite or covellite is due to the presence of ferric salts.

Other minor sulfide minerals such as enargite (Cu_3AsS_4), tennantite ($Cu_6As_2S_7$), and tetrahedrite ($Cu_{12}Sb_4S_{13}$) all appear to have rather limited solubility in ferric salts.

Even low-grade sulfide minerals, unless they are associated with oxidized minerals, are generally not considered for hydrometallurgical processing, since they lend themselves to economic methods of concentration and subsequent treatment by pyrometallurgical methods. However, when they are associated with oxidized minerals, it has been found quite feasible to adapt the combination of acid and ferric salt as a leaching agent. In this type of solvent, the sulfuric acid is the principal solvent for the oxidized constituents and the ferric sulfate for the sulfide portions. Indirectly, varying amounts of iron salts are always present in acid leaching, and as such can facilitate the dissolution of copper minerals. Ferrous sulphate has no oxidizing power, but it is oxidized to the ferric state in the presence of sulfuric acid by air, according to the following reaction:

$$4FeSO_4 + 2H_2SO_4 + O_2 = 2Fe_2(SO_4)_3 + H_2O \qquad (18)$$

LEACHING METHODS

The methods used in leaching may, for convenience in discussing them, be divided into four principal groups: (1) leaching in place; (2) leaching in heaps; (3) leaching by percolation, *i.e.*, sand leaching; and (4) leaching by agitation, *i.e.*, slime leaching. Each has the objective of making a satisfactory contact between the mineral and the lixiviant to obtain maximum extraction at minimum cost.

It is evident that the grade of the material and the association of the mineral with the gangue will be limiting factors determining the choice of the leaching method or combination of leaching methods. Ore too low in grade to justify mining expense might very well be shattered in place and leached over long periods of time with a cheap lixiviant. The other extreme situation is ore of such grade and nature as to justify fine grinding and leaching by agitation. The leaching time involved, and thus the inventory tie-up of metal values in process, will be decreased; but the expense involved in preparing the ore for treatment will be markedly increased as a result of expensive milling costs.

Most ores treated by hydrometallurgical methods are of such grade, *i.e.*, ± 1 per cent, that the economics involved do not permit fine grinding as a preparatory step to leaching. On the other hand, some reduction in size is usually found economical, both from the inventory-time vs. crushing-cost consideration as well as in the over-all recovery of the contained copper.

Leaching in Place

When an ore body containing sulfides is broken or shattered so that the combined action of air, water, and ferric salts act on the exposed sulfides, natural oxidation may take place, the end products being essentially the sulfates of copper and iron. Both are water-soluble. The nature of association of the sulfides determines the speed of reaction, which may take place in a matter of weeks or may require years before oxidation is nearly complete. In either case, it offers a cheap method for extracting copper values in ores too low in grade to make them amenable to treatment by any other method.

The mechanics of the operations consist essentially of shattering to provide passage for the circulation of both air and water on exposed ore surfaces. In this respect, porosity of the gangue may also play an important role in the ultimate disintegration of the ore. Leaching is effected by alternate and intermittent circulation, first of air, followed by water and spent solution from the precipitation process. The main difficulties in the process arise from channeling, which interferes with the even distribution of leach solution over the ore, and a later possibility of slimes and accumulated salts, in time filling the openings and thus also interfering with solution-ore contact. Natural drainage is relied upon for accumulating the leach solution, either through the construction of drainage tunnels under the ore body, or in the case of exhausted or mined-out ore bodies, lower workings in the mine.

The efficiency of the process is difficult to evaluate, in view of the variables of unknown tonnages and content either before, or after, leaching operations.

Leaching in place has been applied successfully in a number of cases, both on mined-out ore bodies and on ore bodies too low in grade to be otherwise considered for economic treatment. The best example of the latter was the treatment by the Ohio Copper Company of approximately 38,000,000 tons of ore, which contained an estimated 0.3 per cent of copper[12]. Production was maintained at approximately 15 tons of copper per day. Among others which have used the method are Eureka Mine, Ducktown[13]; Cronebane Mine, Wicklow County, Ireland[14]; Aznalcollar Mines, Spain[15]; Rio Tinto, Spain[16]; and Ray Mines, Arizona[17].

Heap Leaching

Heap leaching is very similar to leaching in place, in that natural oxidation by air, water, and ferric salts is relied upon to convert sulfide minerals and oxide minerals to water-soluble sulfates. The essential difference lies in the fact that the ore is removed from the mine, and so arranged as to permit more effective contact of both oxidizing agents and lixiviant with the minerals so that maximum extraction of the copper values can be obtained. Low-grade ores can be treated economically in this way, with possibly one limiting factor: ores should contain enough sulfide to oxidize readily, otherwise many years may be required before oxidation of the heap approaches completion. Since the oxidation reactions are exothermic, the heat generated facilitates continued oxidation. Large tonnages are involved; consequently, mining costs have to be low, since the copper will necessarily be recovered over an extended period.

The mechanics of the process consist essentially of building piles of ore in such a way as to provide nearly uniform access for air and leaching solutions to the ore mineral. The ore, without crushing or other preparation, is carefully piled on an area previously provided with culverts and drainage basins. In some instances it may be found advantageous to classify the ore to the extent of placing the coarser ore on the bottom of the heaps and the finer on the top, in order to expedite the circulation of air and solution. Leach solutions are distributed evenly over the section to be leached, and allowed to drain through the heap into the collecting basins provided. The copper, dissolving as copper sulfate, is recovered from the leach solution by cementation on scrap iron. The spent solution, plus make-up water to take care of losses through evaporation, is redirected to the heap. The iron salts present in the precipitated solutions make them more effective as a leaching agent than water alone. The cycle consists of alternate periods of leaching and oxidation. In a large heap certain sections may be undergoing leaching action while other sections are permitted to oxidize.

The process, developed in Spain, has been the principal method of recovering copper at Rio Tinto for hundreds of years. At times as much as 20,000,000 tons of ore have been undergoing treatment simultaneously[18]. The method has also been used at Sacramento Hill, Bisbee, Arizona[19], and on mine dumps at Tyrone, New Mexico[20].

Percolation Leaching

Before discussing the percolation method of leaching, one must necessarily discuss reduction to size. If it were possible to effect satisfactory dissolution of mine-run ore, more economical methods could probably be devised for effecting contact between solute and solvent other than the handling of large tonnages of ore into and out of percolation vats. Although percolation vats of 10,000-ton ore capacity are common, and thus lend themselves to economic methods of handling bulk materials, ever present is the problem of charging the vats with ore, and in turn, after dissolution of the copper has been effected, of removing the residual gangue material to disposal sites.

For purposes of discussion reduction to size can be resolved into the following factors: (1) the grain size of the copper mineral, coupled with its degree of dissemination in the ore; (2) the porosity of the ore; and finally (3) the rapidity with which the copper mineral is attacked by the lixiviant used. Fine grinding would, of course, obviate all of these factors, in assuring maximum contact between copper mineral and lixiviant and also in effecting maximum extraction in minimum time. However, it is acknowledged that fine grinding is the most expensive unit operation in milling. Further, finely divided materials do not as a rule lend themselves to percolation methods of leaching, and therefore necessitate some type of suspension leaching and washing. Suspension leaching is a more expensive unit operation than percolation leaching. Thus, again from economic consideration, one cannot take advantage of what might be considered the optimum conditions for effecting dissolution of the copper mineral.

Reduction to size, then, must be based on the factors noted. It can be said that the larger the ore particle that can be effectively leached in a given time, the less will be the over-all cost of leaching. This fact is evident, since less expense will be involved in reduction to size; circulation of leach solution will be more efficient; and, likewise, washing will be a lesser problem, for less leach liquor will be occluded in the interstices between the ore particles. It is essential that the size of the ore particles to be leached be as nearly uniform as practicable. Leaching time will be determined by the maximum size rather than the average size. Further, excessive fines can interfere with uniform percolation of solutions. In reduction to size, the choice of crushing equipment will be directed to those that in their crushing action tend toward a product of uniform size, coupled with a minimum production of fines.

When fines produced in crushing, or slimes inherent in the ore, seriously interfere with percolation leaching, it is usually found advantageous to classify the crushed product into sands and slimes. The latter portion, which should only represent a small percentage of the whole, can then be treated by suspension methods of leaching.

As a rule, higher-grade ores require crushing to finer mesh sizes for most economical extraction. Dependent on the factors previously noted, mesh size for percolation leaching approximates ± 3/8 inch.

Percolation

Percolation is by far the most widely used method of effecting adequate contact between solute and solvent in commercial hydrometallurgical processes for the recovery of copper from low-grade ores[21]. It utilizes the countercurrent principle with the ore to be leached remaining stationary, as differentiated from most countercurrent methods, where all materials are moving. The charge of ore, confined in a leaching vat, is successively treated with an increasing concentration of leach solution, which may be added as a continuous flow or on a batch basis. Thus, maximum leaching strength first comes into contact with minimum copper concentration in the ore, and as its leaching potential diminishes, it comes in contact with increasing copper concentration in the ore.

If the leach solution enters the vat at the bottom and overflows at the top, the system is known as upward percolation. It is the more common if the flow of solution is continuous through a series of vats. If the solution enters either the top or the bottom, but is withdrawn from the bottom, the system is known as downward percolation, which is the more common method if the batch method is used. A predetermined filling and soaking period, followed by a drain, complete a single cycle. This drained solution then advances to the next vat, and the process is repeated. Solutions are commonly referred to as first advance, second advance, etc., to designate the position in the complete leaching cycle. Dependent upon the solubility of the copper in the ore, a single charge of ore could be given any number of successive leaches with increasing concentrations of leach solution; if, for example, six cycles were necessary for optimum extraction, six charges of ore would be undergoing simultaneous leaching treatment.

Just as important, if not more so, is the effective separation of the occluded leach solution from the final leach residue. Based on the porosity of the residual gangue, the amount of disintegration of the ore that has taken place during leaching, and similar physical characteristics, it may represent as much as 30 per cent of the total copper dissolved. It is, therefore, imperative that as much of this dissolved copper as is practicable be recovered through adequate washing.

Since unlimited use of water for washing purposes is not economically feasible, because of the volumes to be handled and from which the contained copper would have to be recovered, the countercurrent principle of washing is employed. This method, essentially the same as that described for countercurrent leaching, may also be effected on either a continuous or batch basis. In either case, the residual gangue and its occluded solution are successively treated with wash solutions of decreasing copper concentration. The final step is effected with copper-free wash solution. The process consists, accordingly, of a series of dilutions, the effectiveness dependent on the degree of diffusion of the remaining occluded solution and the incoming wash solution in each other.

It is maintained that "piston" displacement, *i.e.*, filling the interstices of the residual gangue with wash solution and then withdrawing by drainage, followed by a similar cycle with wash solutions of successively lesser copper concentration, is more effective than using the same amount of copper-free wash water on a batch basis. In the batch wash, all of the wash solution is added to the residual gangue and its occluded solution and then circulated, followed by a single complete drainage.

Considerations entering the discussion of the relative methods of the two systems hinge largely on the porosity of the residual gangue, and the ability to get adequate diffusion, with or without considerable movement of wash solution. All problems considered, time will be a limiting factor, since it can affect the number of charges of ore in process, and thus in turn influence the investment in capital equipment and inventory tie-up of materials. Very often a combination of the two systems is the more practical, in which case the batch method is used for the final washing, and the advance method of piston displacement in intermediate washing.

Percolation vats are essentially rectangular tanks equipped with perforated bottoms, so constructed as to permit drainage from some given location. Materials of construction vary from plant to plant, as does the method of charging and bedding the ore. Operating details of a typical installation will be discussed in greater detail in a later section of the chapter.

Leaching by Agitation

Leaching by agitation, or slime leaching as it is often called, is limited to those ores, or to that portion of those ores, that because of particle size do not permit free passage of leach solution through the interstices between the ore particles and thus cannot be effectively treated by percolation methods. In some instances, governed by grade and character of the ore, fine grinding and leaching by agitation might be justified for rapid and optimum extraction. This is the case at Katanga, where the ore contains fine slimes, and large quantities of malachite, which in its decomposition with acid results in considerable effervescence resulting from the liberation of CO_2[22]. The copper in the ore, which incidentally is much higher in grade (± 6 per cent copper) than usually encountered in other localities that have adopted a hydrometallurgical process, consists largely of malachite, with minor amounts of azurite, chrysocolla, cuprite, and sulfides. The gangue is siliceous in nature, consisting of shale, sandstone, and quartzite. Sulfuric acid is used as a satisfactory solvent, but as noted the ore is not amenable to percolation leaching. The flow sheet and operating procedure have been covered in the literature[22].

In leaching by agitation, dissolution is effected by keeping the finely divided ore particles in suspension in the solvent. Agitation may be imparted either mechanically or by air, but in either case must be violent enough to prevent settling in the leaching tanks. Dissolution of the ore may be either on a batch or on a continuous basis. In the former, a given charge of ore is agitated with the required amount of leach solution until optimum extraction is obtained. In the latter, ore and leach solution are added simultaneously; but instead of effecting dissolution in a single tank, the ore-solution mixture passes from tank to tank in series until optimum extraction is obtained. Pachuca tanks, with high lifts, are convenient for this type of agitation. Essentially the only difference in the batch and continuous leach is in the feed and discharge mechanics, *i.e.*, a central system versus a number of individual circuits. In either method variations can be made in how, when, and where additions of either ore or leach solution are made.

The separation of residual gangue and leach solution presents a somewhat different problem than is encountered in percolation methods of leaching, where simple draining suffices to separate leach solutions and leach residues. Filtration, while a convenient answer, is usually out of the question because of the tonnage and the nature of the residual gangue. Coupled with this, but of more importance, would be the difficulties involved in getting a satisfactory wash. Adequate washing is even more important than indicated in the discussion of the percolation method of leaching, since an even higher percentage of occluded solution will be tied up with the residual gangue.

Thickeners have become the standard equipment for carrying out both the separation of residual gangue from leach solution and the washing of the occluded solution from the residual gangue. Thickeners by definition take a dilute pulp and resolve it into two products—a clear solution and a thickened pulp. (The relative merits of the various types are not within the scope of this discussion.) When used in series, thickeners provide a convenient method for countercurrent washing. The method is essentially as has been described in percolation washing, but in this instance the residual gangue is also moving. The direction is, of course, countercurrent to the movement of wash solutions of decreasing copper content. The final step in the series for the gangue represents a wash with all make-up water. For improved efficiency in the washing, the thickened pulp from one thickener may be agitated with overflow wash solution from a preceding thickener, a procedure facilitating the diffusion of occluded solution and wash solution, before passing the pulp to the next thickener in the series.

Adequate washing is a very important consideration in all hydrometallurgical processes.

RECOVERY OF COPPER FROM LEACH SOLUTIONS

The methods for the recovery of the copper values from the pregnant leach solutions may be divided into chemical precipitation and electrolytic precipitation. Each method has its inherent advantages and disadvantages.

Chemical Precipitation

Theoretically every metal which lies above copper in the electromotive force series could be used to precipitate metallic copper from a solution of a copper salt. Copper is one of the more noble metals, and thus most of the common metals could be used for this purpose. However, it will also be noted that most of these metals are as valuable as or approach the value of copper. Since in the precipitation the less noble metal goes into solution, the choice of a precipitant becomes rather limited. The only metal which has found commercial importance in this respect is scrap iron, whose acute situation at this writing has aggravated the economic problem of obtaining cheap scrap for precipitation purposes. Consequently, considerable attention is being given to the production of sponge iron by the reduction of iron oxides by various reducing agents such as natural gas, coal, and coke. Reduction is effected in a direct gas-solid reaction, without the formation of a slag. For upgrading of the sponge iron, magnetic separation can be used. Pyrites are receiving considerable attention, both as a source of sponge iron and as a source of SO_2 gas for the production of sulfuric acid. Sponge iron has the advantage over scrap iron of being more rapid and therefore more efficient in its action as a precipitant for copper in solution.

The actual precipitation may be carried out in a number of ways, all aiming for a suitable contact between the iron and the copper-bearing solution. Launders, tanks, and towers are all employed, dependent on the nature of the iron used. The copper precipitates as a loosely adherent, finely divided deposit called cement copper. The process of precipitation is usually referred to as cementation.

According to the precipitation reaction

$$CuSO_4 + Fe = Cu + FeSO_4 \qquad (19)$$

one pound of iron should theoretically precipitate 1.137 pounds of copper, and in actual practice, if sponge iron is used as the precipitant, the requirements approach the theoretical figure (based on the percentage of Fe in the sponge iron). However, if scrap iron is used, from two to three times the theoretical amount is required, the nature of the scrap being the determinant. In turn, the cement copper produced can vary from 50 to 90 per cent copper. For example, if the scrap is badly oxidized, the cements will contain large amounts of iron oxide as an impurity, and even with sponge iron the cements will be relatively impure in consequence of gangue associated with the sponge iron. Free acid and ferric salts in solution can contribute to the consumption of iron according to the following reactions:

$$H_2SO_4 + Fe = FeSO_4 + H_2 \qquad (20)$$

$$Fe_2(SO_4)_3 + Fe = 3FeSO_4 \qquad (21)$$

It will be noted that in the precipitation process, if acid has been used as the solvent, it would not be regenerated. Thus the method is not applicable in a closed circuit with an acid leach. This drawback, coupled with the fact that the cements are not of sufficient purity to be marketable as high-grade copper without intermediate refining, are the major disadvantages of the method. Cements are customarily charged to reverberatory furnaces for smelting, but in some instances of higher purity may be charged to converters or anode furnaces (see also Chapter 41).

Among the advantages of the method are the simplicity of the operation, if a cheap source of iron is available. The method is effective on all concentrations of copper in solution, and particularly on dilute concentrations, from which copper cannot be recovered economically by electrolytic precipitation. Impurities in solution, which could be very detrimental to electrolytic precipitation, do not affect the method.

The cementation process is used successfully to precipitate copper from leach solutions resulting from leaching in place, heap leaching, mine waters, and for stripping wash solution. In each case the copper content is too low to warrant treatment by electrolytic precipitation. It will also be noted that acid has not been used as the solvent.

If the copper in solution is present as a cuprous salt, it would be possible to precipitate two equivalents of copper with one equivalent of iron. An excess of cement copper in the presence of chloride ions will reduce copper sulfate or cupric chloride to the insoluble cuprous chloride according to the following reactions:

$$Cu + CuSO_4 + FeCl_2 = 2CuCl + FeSO_4 \qquad (22)$$

$$Cu + CuCl_2 = 2CuCl \qquad (23)$$

The reaction is quantitative if a sufficiently large excess of cement copper is used. Cuprous chloride is soluble in a strong ferrous chloride brine, from which copper can be precipitated according to the following equation:

$$2CuCl + (FeCl_2\ \text{brine}) + Fe = 2Cu + FeCl_2 \qquad (24)$$

The necessary cement copper and brine can be recirculated in closed circuit.

This adaptation is used at Chuquicamata to precipitate copper from waste electrolyte[23]. It should be noted in the reactions, although the copper has been precipitated from an "ous" salt, that the net consumption of iron is equivalent to precipitation from the original "ic" salt, since in the reduction to insoluble cuprous chloride an equivalent of metallic copper has entered the cuprous salt, which in turn has to be reprecipitated from the brine solution.

Hydrogen sulfide has been suggested as a precipitant for copper from solution; but because of its noxious characteristics, coupled with the fact that the precipitated cupric sulfide would be a product bulky and difficult to handle, the suggestion has not had commercial adaptation[24]. The sulfide would also require smelting to recover the contained copper.

Sulfur dioxide has also been suggested as a precipitant, since under pressure it will reduce copper sulfate to metallic copper according to the following reaction[25]:

$$CuSO_4 + SO_2 + 2H_2O = Cu + 2H_2SO_4 \qquad (25)$$

It will be noted that in the precipitation two equivalents of acid are generated per equivalent of copper precipitated. The reaction is not quantitative, which is one of the principal objections, combined with the disadvantage that heat and pressure are required to obtain a completion of approximately 70 per cent.

Ammoniacal Precipitation

As previously noted, copper dissolved in ammoniacal solution forms the complex cupric ammonium salt, which hydrolyzes readily unless an excess of free ammonia is present. Thus, through simple heating to drive off the excess ammonia, the complex can be converted to the copper salt. If carbonate has been used for the negative radical, the final copper product will be copper oxide, as $CuCO_3$ will also decompose in solution. This has been the principal advantage of using the carbonate as the negative radical, since both ammonia and CO_2 can be recovered in scrubbing towers to regenerate the leach solution.

Electrolytic Precipitation

Electrolysis, using insoluble anodes, is the most widely employed method for the precipitation of copper from sulfate solutions. Among the advantages of the method is the recovery of a product that is equal in purity to the best refined cathode copper. Further, in the process an equivalent of sulfuric acid is regenerated for each equivalent of copper produced. Thus the method is adapted to a closed circuit. The process is generally referred to as electrowinning as differentiated from electrorefining.

Electrolysis. Electrolysis can be considered as consisting of two equivalent oxidation and reduction reactions, the oxidation taking place at the anode, the reduction taking place at the cathode. In electrorefining the mechanics of the reactions are simplified to the extent that the oxidation of an equivalent of metal at the anode, proportional to the amount of current passing (Faraday's law) is accompanied by the reduction of the same equivalent amount of metal ion at the cathode. Disregarding behavior of impurities, the composition of the electrolyte remains unchanged, and the net cell reaction, ideally, is the anodic corrosion and cathodic deposition of equal amounts of the same metal. Because there is no decomposition potential involved, the voltage required is mainly that needed to overcome ohmic resistance of the electrolyte, or $E = IR$. The process takes advantage of factors which influence resistance, such as concentration, temperature, etc., and thus optimum electrolytes and electrolyzing conditions are chosen.

In electrowinning, the net cell reactions are also equivalent oxidation and reduction reactions, but in this instance, since insoluble anodes are used, the oxidation and reduction does not take place on equivalents of the same material. Further, then, the source of material undergoing reaction must be the electrolyte.

Specifically, for the electrowinning of copper from an electrolyte containing the copper as a sulfate solution, the $CuSO_4$ must undergo the oxidation-reduction reactions. This again represents the ideal condition, with no complication of impurities that could be present along with the $CuSO_4$ in solution. If $CuSO_4$ is considered to ionize as Cu^{++} ions and SO_4^{--} ions, the reaction at the cathode is

$$Cu^{++} + 2(e) = Cu \qquad (26)$$

This reduction reaction is equivalent to that taking place in electrorefining. At the anode the oxidizing reaction is

$$SO_4^{--} - 2(e) = SO_4 \qquad (27)$$

The sulfate radical is not stable and immediately reacts with water in the electrolyte to form sulfuric acid and oxygen according to the following reaction:

$$SO_4 + H_2O = H_2SO_4 + \tfrac{1}{2}O_2 \qquad (28)$$

It will be noted that in the electrolytic decomposition of a solution of $CuSO_4$ the solution will be depleted of one equivalent of copper for each equivalent of copper deposited at the cathode, the solution will be enriched by the formation of one equivalent of sulfuric acid, and one equivalent of oxygen will be liberated at the anode.

The voltage required for the electrolysis is not the simple *IR* drop as noted for electrorefining but includes, in addition to the *IR* requirement, enough added potential to decompose the $CuSO_4$, plus potential to liberate the O_2 formed at the insoluble anode. The latter is referred to as the gas overvoltage.

Since the net cell reaction is known, the reaction potential can be calculated.

$$CuSO_4 + H_2O = Cu + H_2SO_4 + \tfrac{1}{2}O_2. \quad \Delta H = +\ 56{,}620 \text{ cal} \qquad (29)$$

The reaction being endothermic, electrical energy equivalent to 56,620 cal of chemical energy must be supplied for the decomposition of one mole of $CuSO_4$. A close approximation of this potential can be obtained from Thomson's rule, *i.e.*, $E = U/nJF$, where E is the reaction potential, U the heat of reaction in calories, n the number of equivalents, $F = 96{,}500$ coulombs, and J is the factor for converting joules to calories (1 joule = 0.239 cal). Since in any given reaction not all of the electrical energy is necessarily converted to chemical energy or vice versa (*i.e.*, some energy may be absorbed or given up to the surroundings), Thomson's rule is not strictly accurate. The correct formula for calculating the reaction potential is the Gibbs-Helmholz equation: $E = U/nJF + T\ dE/dT$. It is essentially the Thomson rule with a correction factor in which T is the absolute temperature, and dE/dT the temperature coefficient.

The decomposition potential, also capable of measurement, has, for a normal solution of $CuSO_4$, been determined as 1.49 volts[26]. The decomposition potential includes a minimum overvoltage in addition to the reaction potential.

Overvoltage. The potential necessary to liberate the oxygen at the anode is referred to as the oxygen overvoltage. Various theories have been advanced for the phenomenon, but the immediate concern in the electrowinning of copper is its effect on the voltage requirement for the electrolysis. Oxygen overvoltage on an insoluble anode can be a considerable factor, varying from 0.5 to 1.0 volt[27], dependent upon the nature of the electrolyte, the temperature, the composition and condition of the anode, and the anodic current density. Two important factors which contribute to lower gas overvoltage are lower anodic current density and higher electrolyzing temperature.

The summation of the reaction potential, the overvoltage, and the *IR* drop through the electrolyte will vary from 1.8 to 2.1 volts. This potential can be compared to the 0.2 to 0.3 volt required in electrorefining.

Ampere Efficiency and Composition of Electrolyte. As repeatedly indicated, hydrometallurgical processing cannot always take advantage of chemical principles to improve dissolution, etc., because they adversely affect the over-all cost considerations. This again becomes evident when consideration is given to the actual electrolytic precipitation of the copper contained in the leach solutions. Higher acid and copper concentrations in the solutions lead to higher conductivity, and at the same time permit a greater depletion of copper per unit of leach solution, without too adversely affecting the ampere efficiency. However, in consequence of complications in the leaching cycle, such as effective washing, corrosion problems, and the like, the feed to the electrolyzing cells rarely contains over 60 pounds of copper per ton of solution. A depletion of only about 20 per cent in the copper content is effected in the electrolysis.

The reason for this becomes evident if attention is given to the fact that as the copper concentration decreases during electrolysis the free acid concentration increases. Thus the hydrogen ion concentration can increase to the point where, as a result of diminishing copper ion concentration, hydrogen and copper can be co-deposited at the cathode. The net outcome is a loss of ampere efficiency as concerns the deposition of copper. In electrorefining, where optimum electrolytes can be chosen, ampere efficiencies are usually well over 90 per cent; in electrowinning, efficiencies as low as 75 per cent are not uncommon.

Certain impurities in solution may also adversely affect the electrolysis. Among those with deleterious effects, and more commonly encountered in leach solutions, are ferric iron, nitrates, molybdenum, and chlorides. Most of the other impurities encountered in the solutions are relatively harmless in effect on electrolysis or on the purity of the cathode copper.

Ferric iron is probably the most harmful impurity in its influence upon ampere efficiency. In processes that require ferric salts for the dissolution of sulfide minerals, the deleterious effects are of more concern. The effect of ferric ion is essentially chemical, in that it will dissolve copper, in which dissolution of the cathodically deposited copper the ferric ion is reduced to the ferrous ion. Equations representing the action follow:

$$2Fe^{+++} + Cu = 2Fe^{++} + Cu^{++} \tag{30}$$

$$Fe_2(SO_4)_3 + Cu = 2FeSO_4 + CuSO_4 \tag{31}$$

In turn, ferrous ion can be oxidized at the anode to re-form the ferric ion

$$Fe^{++} - (e) = Fe^{+++} \tag{32}$$

However, unless the ferrous ion concentration is very high, the oxidation of the sulfate ion will take precedence, as it requires a lower potential. Ferrous ion is, therefore, generally considered harmless when present.

Indirectly, the deleterious effect of nitrates in solution is due to their ability to assist in the anodic oxidation of ferrous ion to ferric ion. The harm is more pronounced when small amounts of molybdenum are present in solution. Molybdenum acts as a catalyst for the reaction. The deleterious effect of chlorides on electrolysis is usually due to corrosion of the anodes, and can also result in the liberation of chlorine in the tankroom atmosphere.

Purification. The most effective way to control ferric iron content of the electrolyte is by prior reduction to ferrous iron. SO_2 gas passed through a solution containing ferric sulfate will effectively reduce the ferric iron content to about 0.4 gram per liter[28]. The reaction follows:

$$Fe_2(SO_4)_3 + SO_2 + 2H_2O = FeSO_4 + 2H_2SO_4 \tag{33}$$

Sulfuric acid generated in the reaction can be considered advantageous, since make-up acid is necessary to take care of losses of SO_4 ion, inherent in the leaching process.

Diaphragm cells have been suggested as a possibility, but since they increase voltage requirements and introduce mechanical difficulties, this type of cell has not found commercial use[29].

Cement copper will also reduce ferric sulfate to ferrous sulfate by the same reactions noted for the dissolution of cathode copper. Indirectly, the use of cement copper for the reduction will still result in a loss of ampere efficiency, because the copper which has gone into solution in the reduction, ultimately, has to be recovered from solution. The method finds adaptation when solutions have to be purified to chlorides. Cement copper will effectively reduce cupric chloride to the very insoluble cuprous chloride. The reactions and method of recovery of the copper from the cuprous chloride precipitate have been discussed under chemical precipitation.

When nitrates or molybdenum are troublesome, the only effective method of control or elimination from the circuit is by stripping and discarding a portion of the electrolyte. Maintaining reducing conditions in the electrolysis with SO_2 gas minimizes the oxidizing effects of these impurities, but in no respects is it a cure-all. These impurities are also particularly corrosive on solution lines, pumps, etc. Stripping and discarding electrolyte also takes care of such impurities as the sulfates of aluminum, magnesium, calcium, and sodium, all of which have a tendency to built up in closed circuit. Although none are detrimental to electrolysis, they can cause operating difficulties when solutions approach saturation, for they may crystallize out in solution lines, etc. Chemical precipitation, as previously discussed, is used in stripping.

Electrodes. The electrodes used in electrowinning are copper starting sheets for cathodes and some type of insoluble anode to serve as a conductor to bring the current to the electrolyte. To be effective, the insoluble anode should neither react chemically with the electrolyte nor be oxidized either through the action of the current or the oxygen liberated at the anode. Further, its overvoltage characteristics should be at a minimum. Among the materials that meet these requirements in some degree, while still exhibiting the requisite mechanical characteristics, are antimonial lead, copper-silicon alloys, magnetite, and alloy cast irons. Antimonial lead has found the most favor, particularly where chlorides and nitrates pose no particular problems. Anodes may be cast or of rolled sheet and are equipped with suitable contacts and supporting lugs. Grid construction is often used to cut down both on the weight of the anode and to lower the anodic current density. The cathode sheets are similar to those used in electrorefining, and cell construction and electrical hookups are also similar to the multiple system as used in electrorefining. For this reason they will not be discussed further.

Power. Because of the much higher voltage requirements, combined with generally lower ampere efficiency, the power requirements for electrowinning are from 8 to 10 times as much as required in electrorefining; however, power costs are largely offset by decreased labor costs in the electrolyzing division. Cathode handling could be considered a standoff with electrorefining; but anode handling and scrap remelting, which represent a major cost item in electrorefining, are at a minimum in electrowinning, since the anodes are insoluble and may have a service life of 10 years. Further, there are no anode muds or slimes to deal with, which again are major cost items in the operation and maintenance of an electrorefining tankroom. The above considerations are merely mentioned to call attention to differences in operation rather than to promote discussion on the relative merits of electrowinning and electrorefining, as each has its specific application.

EXAMPLES OF PRACTICE

Inspiration Consolidated Copper Company[30]

To illustrate some of the principles previously discussed and to make note of some of the equipment used in the hydrometallurgical processing of a low-grade copper ore, the operations of the Inspiration Consolidated Copper Company, at Inspiration, Arizona, have been chosen for detailed discussion. The Inspiration plant exemplifies both percolation and slime leaching; further, it utilizes both chemical and electrolytic precipitation for the recovery of copper from solution. The ore is complex, containing oxidized and sulfide copper minerals, and thus to obtain satisfactory dissolution both sulfuric acid and ferric sulfate are employed in the leach solutions.

The plant was placed in operation in October, 1926, at a rated capacity of 9,000 tons of ore per day. Leaching was to have been by percolation only; however, a peculiarity of the ore, which was evidenced early in the Inspiration operations, was that natural slimes interfered seriously with percolation leaching to the extent that extraction was very erratic. It was found that these natural slimes were concentrated in the fines from coarse crushing. By classifying, an approximate 80 per cent separation could be obtained, resulting in the removal of about 600 tons of slimes per day, which in view of their copper content justified separate treatment. As the fines are amenable to flotation without intermediate grinding, available sulfides are removed previous to leaching. Sulfuric acid is a satisfactory solvent on the flotation tails, which are treated by agitation in a separate circuit. The present capacity of the plant is approximately 11,000 tons of ore per day, with about 8 per cent being treated as slimes. Production of copper varies with the heads, since percolation leaching capacity is fixed at 10,000 tons per day.

The Ore. The principal sulfide mineral in the ore is chalcocite, and the oxidized minerals are mainly chrysocolla, malachite, and azurite. None of these minerals is acid-forming in closed circuit; consequently, make-up acid to take care of losses must be supplied from other sources. The ore likewise contains little soluble iron. It presently is running about 1 per cent copper, with the sulfide accounting for ±65 per cent of the total. The oxidized minerals are readily soluble in dilute sulfuric acid, but for satisfactory dissolution of the copper, the comparatively high sulfide content requires the strong oxidizing action of ferric sulfate.

The ore as received from the mine is delivered to the primary crushing division, which consists of gyratory crushers and horizontal-shaft Symons disk crushers. A reduction in size to minus 1½ inches is obtained. The coarse-crushed ore is delivered by belt conveyor to storage bins of 10,000-ton capacity, from which it is drawn by conveyor to a bank of eight Hummer vibrating screens, equipped with ¼-inch screens. The minus ¼-inch material, which, as has been noted, contains the bulk of the natural slimes, is classified in two 25-foot Dorr bowl classifiers. The overflow from the classifiers, amounting to ±8 per cent of the original ore, is directed to the flotation circuit, with subsequent slime leaching of the tails. Sands from the classification are directed to the percolation leaching division.

Oversize from the screening operation is directed to four sets of 78-inch by 24-inch face Traylor rolls. Two sets are operated as fine rolls, one set as a coarse roll, leaving one set as a spare. The discharge from all rolls is delivered to sixteen Hummer screens equipped with ⅜-inch screens. Undersize from these join the classifier sands as feed to the percolation leaching vats, the oversize returning in closed circuit to the two fine rolls. The coarse rolls are set at ⅝ inch and the fine rolls at 5/16 inch. The crushing of 10,000 tons through this division requires about 10 hours.

The conveyor delivering crushed ore to the percolation tanks is equipped with a weightometer, and a bucket sampler cuts the discharge stream. Thus, accurate weights and samples for each charge are obtained for metallurgical balances.

Leaching Equipment. There are thirteen concrete, lead-lined leaching tanks, each 175 feet long, 67.5 feet wide, and 19.5 feet deep, with a capacity of 10,000 tons of dry ore per tank. The 7-pound chemical lead lining is protected by a covering of 2-inch planks, held in place by vertical timbers. The filter bottom, protected by 4-inch by 6-inch timbers laid on edge, is made of 2-inch planks, perforated with fifteen ⅜-inch holes per square foot of surface. A 14-inch lead pipe burned to the lead lining serves as the single charge and drainage point for all solution. It is situated at the end of the tank, opposite the overflow, and between the filter bottom and the tank bottom. Satisfactory drainage is obtained, as the tank bottom slopes slightly toward the center as well as toward that end.

Served with a single feed conveyor, the thirteen leaching tanks are arranged in a single row. A spreader bridge (equipped to move from tank to tank as needed) spans the bank of tanks. A tripper discharges the crushed ore from the feed conveyor to a cross conveyor on the spreader bridge. An automatic reversing tripper travels on the cross conveyor, and at each reversal of the tripper, the bridge moves forward 2½ feet until it reaches the edge of the tank. At that point, bridge travel is reversed and the cycle repeated. In this manner, ore is bedded evenly over the entire area, the bed rising approximately 3 feet for each pass of the bridge.

Leaching

The leaching method used is countercurrent, upward percolation. The ore, after bedding, is first covered with a solution high enough in acid to prevent neutrality at any point in the charge, the purpose being to avoid precipitation of bulky basic iron salts from the leach solutions, which in turn, due to difficulties in washing, could result in higher copper losses in the residue tails. Approximately 200,000 gallons of solution is required to cover a charge.

Percolation of solution is upwards, each tank being provided with a vertical screw-type lead pump, which receives the overflow solution from the preceding tank and pumps it underneath the filter bottom and up through the ore charge. The solution overflows the tank into a launder, connected to the suction intake of the pump serving the next tank. The rate of circulation in each tank is approximately 2,400 gallons per minute.

Eight tanks are under leaching contact at all times; three are being washed, one tank is being filled, and another excavated, 13 days completing the cycle. The spent electrolyte from the electrolytic precipitation, in which sulfuric acid and ferric sulfate have been regenerated, and to which the required amount of new acid has been added to take care of losses, is delivered to the oldest ore under leaching contact. The leach solution travels from tank to tank in series, and in its passage loses solvent potential, at the same time increasing in copper content, until it emerges from the newest ore, to return to the electrolyzing division for precipitation of a part of the contained copper and regeneration of the leach solution.

One of the principal differences between operations as carried out at Inspiration and other leaching plants lies in the deliberate effort to maintain a high ferric sulfate concentration in the face of its known detrimental effect on ampere efficiency in the subsequent electrolytic precipitation of the copper. The high ferric sulfate concentration is necessary to secure satisfactory dissolution of the chalcocite in the cycle noted. General practice is to hold the average strength of ferric sulfate at 7.5 grams per liter, the maximum being about 11 grams per liter and the minimum about 5 grams per liter.

Washing. Washing constitutes one of the most important phases in the operation, the necessity for which may best be visualized when it is noted that a completely drained charge of ore contains about 11 per cent moisture as occluded solution. The copper concentration of this occluded solution is approximately equivalent to that in the return electrolyte, or about 30 grams per liter. This, then, represents 10,000 tons @ 11 per cent @ 30 grams per liter, or 66,000 pounds of copper, in turn equivalent to upwards of one-third the daily production.

Three days are utilized for washing, and every effort is bent toward removing as much of the dissolved copper as practicable. Ten washes are used, the first five, called regular washes, are advanced progressively, the first wash solution joining the main solution system, the second wash becoming the first wash on the next charge in the cycle, and so on. Wash solution, for these five countercurrent advances, is the spent solution from the cementation division, called iron-launder stock solution, which, as noted, finally joins the main solution system.

Four more washes follow with iron-launder stock solution, of which the solution from the first three are cycled to the cementation launders. The fourth wash solution returns to iron-launder stock solution. The tenth and final wash is with fresh water, the solution also joining the stock solution.

A batch wash is normally used; the wash liquor is added, circulated, and then drained before a succeeding wash takes place. As the only plant discard is moisture in the final tailings, wash-water volumes and wash-solution advances are watched very carefully, so that all fresh water may be added as a final wash.

Tailings Disposal. After a tank of ore has been leached, washed, and drained, the gangue residue or tailings are disposed to waste. For this removal a Wellman-Seavers-Morgan bridge-type excavator is used. The bridge travel is across the entire bank of 13 tanks, and the bucket carriage travel is along the length of the tank. The bucket can handle about 17 tons of wet tailings per cycle, consisting of loading, traveling to the end of the bridge, and discharging through a hopper into air-dump, standard-gage railroad cars. Three buckets usually constitute a carload, and from 6 to 10 cars a train. Two 8-hour shifts are required to excavate a tank. At the present time there are about 65,000,000 tons of tailings on the dump.

Cementation Launders. Nine double-section cementation launders, 60 feet long, 20 feet wide, and 5 feet deep, are used for the chemical precipitation of the copper contained in the wash solutions. Baled tin cans (92.5 per cent iron) serve as the precipitant. A function of this division, in addition to recovery of copper from solution, is to furnish the required iron concentration for the leaching division, since the ore contains little soluble iron. The iron consumption per pound of copper precipitated is about 1.8 pounds. This figure may be considered high, but can be accounted for by the high percentage of acid and ferric sulfate in the solutions going to precipitation. To conserve acid, the solution flow is in series, and the rate of travel is regulated so that some copper remains in the final tails. Since the tails subsequently serve as wash solution, the contained copper does not represent a loss. All copper precipitated chemically does represent a loss in acid to the system. Further, acid concentration in the leaching circuit is always held higher than necessary for the extraction of the oxide copper to avoid neutrality at any point in the charge, and subsequently to prevent the precipitation of basic iron salts. This high acid concentration causes an added acid consumption. Sulfuric acid of 66° Bé, produced locally in contact acid plants, is added as required to the spent electrolyte. Consumption based on 100 per cent acid strength amounts to 21.5 pounds per ton of ore treated. Operating data for a typical month's operation in the leaching division are included in Table 13-1.

Slime Treatment. The slimes, from the classification of the primary crushing undersize, are first treated by flotation to recover the bulk of the sulfides, and the resultant flotation tailings, after thickening, are then treated by agitation with sulfuric acid to recover the oxide copper.

The agitation leach is conducted in series, in three mechanically agitated, lead-lined tanks. Four 150-foot traction Dorr thickeners are used for washing the leach pulp. Iron-launder stock solution, repulped with the spigot from the third Dorr thickener in the series, serves as the wash solution. Overflow from the fourth thickener, repulped with spigot from the second thickener, becomes the feed for the third thickener. The cycle continues until the overflow from the first thickener, containing about 3 grams of copper per liter, is cycled to the cementation division for the recovery of the contained copper. Spigot from the fourth thickener is disposed to waste. An over-all recovery of about 97 per cent of the dissolved copper is effected.

Electrolytic Precipitation. The electrolyzing division consists of 120 commercial tanks and 16 starting-sheet tanks. Current is supplied by six motor-generator sets, having a combined capacity of 36,000 amp at 320 volts. All generators supply a single circuit, arranged in a U, since the tanks are arranged in two parallel rows. Since this arrangement is conducive to tank short circuits, precautions are taken to minimize this possibility.

Starting Sheet Division. As leaching conditions vary from time to time, the resultant solutions are not always suited to the production of good starting sheets. This very important consideration has led to the incorporation of a small electrolytic refinery for this express purpose. It consists of 16 tanks of regulation size, each tank having a capacity of

68 blanks (136 starting sheets) and 69 anodes. The blanks are refinery type, of rolled copper, fitted with grooves on each side and bottom, to produce clean-cut sheets. The finished sheet is 44 inches long and 42 inches wide. After being equipped with loops (cut sheet, 20 inches long and 4 inches wide before looping), the finished sheet has a submerged area 42 by 42 inches, which allows the entire loop and punching to be above the electrolyte level in the commercial cells. A 24-hour deposit of copper at a current density of from 14 to 16 amp per square foot gives a starting sheet weighing about 13.0 pounds before looping.

Blister anodes, supplied by the International Refinery, weigh on the average 1,250 pounds. They are suspended on 6-inch centers. Since the plant is not equipped to work up scrap, the anodes from an entire tank are scrapped at one time for shipment.

The electrolyte carries 40 grams of copper and 160 grams of H_2SO_4 per liter. It is circulated at the rate of 15 gal per tank per minute to two hot wells, which maintain an electrolyzing temperature of about 55°C. Bleeding refinery electrolyte to the commercial division, as required, avoids accumulation of impurities. Refinery slimes are periodically washed to settling tanks, dried, and shipped for their precious-metal values.

Commercial Division. The commercial division consists of 120 tanks, 33 feet long, 4 feet wide, and 4 feet 3 inches deep. In each tank are 96 cathodes and 97 insoluble anodes (suspended on 4-inch centers), or a total of 11,520 cathodes and 11,640 anodes. Anodes are of cast construction from antimonial lead containing 8 per cent antimony. They are ½ inch thick and have a submerged area 38 by 40 inches. Being of somewhat smaller cross section than the starting sheets, they minimize beading on the edges of the cathodes.

Starting sheets are straightened, threaded on copper supporting bars, and painted. Painting is done at the solution line with an acid-resisting paint, as it was found that sheets tended (in about five days) to cut off at the solution line. All starting sheets are placed in the tanks singly by hand. Each cathode is restraightened after the first 24-hour deposit, and at regular intervals all cathodes are checked with a millivoltmeter for poor contacts or short circuits. Optimum results are obtained when cathodes weighing about 100 pounds are pulled. Cathode handling by overhead cranes, washing, and racking are typical of most refineries.

The 120 commercial tanks are divided into eight banks of 15 tanks each, the electrolyte flowing from bank to bank in series. The rate of flow in each bank is 1,500 gal per minute or 100 gal per minute per tank. Since the amount of copper dissolved from the ore varies considerably, the copper, acid, and ferric sulfate contents of the electrolyte cannot be held at some predetermined optimum amounts. Thus, the entire tankroom operations vary somewhat on a day-to-day basis.

Since ferric sulfate is essential for the dissolution of the chalcocite in the ore, it can be considered that the electrolysis serves two functions: reduction of the copper at the cathode, and oxidation of ferrous ion to ferric ion at the anode. Although ferric sulfate, as pointed out, is very detrimental to ampere efficiency, this sacrifice must be made to assure regeneration of a suitable solvent for the ore minerals. An examination of Table 13-1 will show how damaging the ferric iron concentration is to cathodic ampere efficiency. Thus in Section 1, which represents the first bank of 15 cells, and which receives the pregnant leach solution, the ferric iron concentration is 3.7 grams per liter (22.1 grams per liter total iron) and the ampere efficiency 84 per cent. As the ferric iron concentration increases, through anodic oxidation of the ferrous iron in solution, in the passage of the electrolyte in series from bank to bank, the ampere efficiency decreases, so that in the last bank of cells it averages 68 per cent. The ferric iron concentration in the same passage increases to 11.3 grams per liter.

Current efficiency for the operation is reported as two independent figures, cathode efficiency and anode efficiency. The cathode efficiency is the customary ratio of actual metal deposited to that theoretically possible, whereas the anode efficiency is the ratio of the weight of ferrous sulfate oxidized to the weight of ferrous sulfate which could theoretically be oxidized.

Operating data, including such figures as current density, ampere efficiency, etc., for a typical month's operation are given in Table 13-1, which also includes other metallurgical data.

TABLE 13-1. INSPIRATION CONSOLIDATED METALLURGICAL RESULTS—APRIL, 1951

Feed	
Ore charged, tons	336,243
Moisture, per cent	7.504
Ore charged, tons dry	311,011
Oxide copper, per cent	0.366
Sulfide copper, per cent	0.652
Total copper, per cent	1.018
Ore on 4 mesh, per cent	22.4
Ore through 20 mesh, per cent	29.2
Tailings Excavated	
Moisture, per cent	10.713
Oxide copper, per cent	0.010
Sulfide copper, per cent	0.152
Total copper, per cent	0.162
Extraction, oxide copper, per cent	97.286
Extraction, sulfide copper, per cent	76.687
Extraction, total copper, per cent	84.086
Copper dissolved per ton of ore, pounds	17.120

TABLE 13-1. INSPIRATION CONSOLIDATED METALLURGICAL RESULTS—APRIL, 1951 (*Cont'd*)

Solutions	
Acid solution advance, gal. per minute	2,400
Copper solution to tank house, gal. per minute	*2,400*
Copper solution to tank house, sp. gr.	1.214
Copper solution to tank house, grams copper per liter	36.60
Copper solution from tank house, grams copper per liter	31.0
Copper solution to tank house, grams acid per liter	18.6
Copper solution from tank house, grams acid per liter	28.4
Copper solution to tank house, grams total iron per liter	22.1
Copper solution to tank house, grams ferric iron per liter	3.7
Copper solution from tank house, grams ferric iron per liter	11.3
Copper solution to tank house, °C	35.5
Copper solution from tank house, °C	41.7
Tank House, Commercial Division	
Commercial copper produced, pounds	4,427,392
Average voltage, anode to cathode	2.28
Average current density, amp. per sq. ft.	11.40
Number of tanks in operation	120
Tank House, Starting-sheet Division	
Number of tanks in operation	15
Number of starting sheets produced	55,907
Average weight of starting sheet, pounds	12.7
Soluble anodes received, pounds	1,458,882
Scrap anodes shipped, pounds	294,772
Miscellaneous Data	
Electrolytic copper shipped, pounds	5,246,579
Gross kw hr A.C. to substation	5,713,500
Gross kw hr D.C. to tank house	5,256,420
Conversion efficiency, per cent	92.0
Kw hr per pound of copper, A.C.	1.260
Ampere efficiency, cathode, per cent	75.76
Ampere efficiency, anode, per cent	77.24
Electrolytic copper, per cent purity	99.92
Iron consumed per pound of copper precipitated in launders	1.857
Copper precipitated per ton of ore, pounds	3.728
Copper in solution to launders, grams per liter	4.6
Copper in solution from launders, grams per liter	0.44
Moisture in ore, gallons per ton of ore	18.00
Fresh water added as wash, gallons per ton of ore	23.5
Total incoming water, gallons per ton of ore	41.5
Moisture in tailings, gallons per ton of ore	25.7
Evaporation and other losses, gallons per ton of ore	15.8
Feed to flotation, oxide copper, per cent	0.841
sulfide copper, per cent	0.505
total copper, per cent	1.346
Tailings from flotation, oxide copper, per cent	0.833
sulfide copper, per cent	0.176
total copper, per cent	1.009
Extraction, oxide copper, per cent	1.78
sulfide copper, per cent	65.36
total copper, per cent	25.65

TABLE 13-2. AVERAGE TANK-HOUSE RESULTS

Section	Current Density	Voltage	Ampere Efficiency	Ferric Iron (Grams per Liter)	Temperature (°C)
1	11.4	2.35	84.0	3.7	35.5
2	11.4	2.31	81.0		
3	11.4	2.29	79.0		
4	11.4	2.28	78.0		
5	11.4	2.27	78.0		
6	11.4	2.26	72.0		
7	11.4	2.25	70.0		
8	11.4	2.23	68.0	11.3	41.7
Average	11.4	2.28	75.76		

BRIEF SUMMARY OF OTHER PLANTS

Chile Exploration Company[31]

The operations of the Chile Exploration Company at Chuquicamata constitute the largest hydrometallurgical processing plant in the world. The plant is rated at a monthly capacity of 1,400,000 tons of ore, which, dependent on the head assays, represents a production of from 20,000 to 28,000 tons of electrolytic copper per month.

The ore mineral, associated in a highly altered granitic gangue, is principally brochantite [$Cu_4(OH)_6SO_4$]. It is readily soluble in dilute sulfuric acid and thus lends itself to hydrometallurgical processing. Sufficient sulfuric acid is recovered from the sulfate portion of the mineral to maintain acid requirements for the entire leaching process. The so-called "oxide" ore contains approximately 1.7 per cent copper, of which about 90 per cent is oxide copper and 10 per cent sulfide copper. Recoveries of 98 per cent of the oxide copper and 40 per cent of the sulfide copper are obtained in a dilute sulfuric acid leach. Mixed ore containing about 40 per cent of the contained copper as a sulfide (largely chalcocite, Cu_2S) is leached separately with a ferric sulfate-sulfuric acid leach solution. Extraction of approximately 70 per cent of the sulfide copper is obtained, coupled with the usual extraction on the oxide portion. Increasing amounts of this type of ore, coupled with higher percentages of sulfide copper, have led to the recent adoption of a combination leach-flotation process.

The ore is mined by open-pit methods, crushed to ± 0.371 inch, and leached in vats of 11,500-ton capacity. The leach solution is spent electrolyte assaying approximately 58 grams sulfuric acid per liter, 15 grams copper per liter, and 2.5 grams iron per liter. The pregnant leach solutions assay approximately 25 grams sulfuric acid per liter and from 20 to 26 grams copper per liter. The leaching method used is batch percolation. Mechanical handling of the large tonnages of ore, solutions, tails, etc., is typical of other hydrometallurgical operations.

Small amounts of chloride and nitrate salts present in the ore dissolve with the copper, and must be controlled to avoid difficulties in the subsequent electrolytic precipitation of the copper from the leach solutions. Chlorides are effectively controlled by precipitation with cement copper to form insoluble cuprous chloride. The chemistry of this purification and the recovery of the copper from the cuprous salt have been discussed. This purification also indirectly serves a second function, in that it reduces ferric sulfate to the less harmful ferrous sulfate. The chemistry of this reduction has also been discussed.

The deleterious effects of nitrate ions present in the electrolyte are partially controlled through stabilization of the electrolyte by the addition of SO_2 gas to the cells. The small amounts of sulfurous acid, so formed, inhibit the decomposition of nitrates. An excessive build-up in *the circulating load of nitrates is circumvented by systematically bleeding* and chemically stripping some of the electrolyte. This bleeding also takes care of any build-up of calcium, magnesium, sodium, and aluminum salts in the circuit.

The copper is recovered from solution by electrolytic precipitation. Chilex anodes, an alloy of copper and silicon developed by Chile Exploration, and lead-antimony anodes are used. Chilex anodes, though more resistant to the corrosive action of the solution and current, especially of nitrate ions, require more power per pound of copper produced than do the lead-antimony anodes. With better control of impurities in the electrolyte, the lead-antimony anodes are proving more favorable. Ampere efficiencies of from 85 to 92 per cent are obtained. Efficiency varies somewhat with current density, which ranges from 7 to 18 amp per square foot, as demanded for output.

Andes Copper Mining Company[32]

For the treatment of ores originating in the oxidized zones at Potrerillos, Chile, the Andes Copper Mining Company utilizes a 6-day countercurrent, combination upward and downward percolation, sulfuric acid leach, and a 1-day, countercurrent wash. The operation is unique in that all of the leach solution is purified by the addition of 200-mesh lime. Iron, alumina, arsenic, and other impurities are precipitated in the purification and eliminated from the circuit. Any free acid present is neutralized and lost to the system, so that the acid consumption is unusually high, amounting to about 63 pounds of 63° H_2SO_4 per ton of ore treated. Sulfuric acid is produced locally from SO_2 in roaster gases from the pyrometallurgical smelting of sulfide ores.

All wash solutions are also treated with excess lime to recover the contained copper as $CuCO_3$. The sludge from this precipitation is reused in the initial lime purification of the leach solution.

Since slimes interfere with the percolation leach, it has been found advantageous to remove them and treat them separately with an agitation leach.

Copper contained in the leach solutions is recovered by conventional electrolysis.

Calumet & Hecla Consolidated Copper Company[33]

The Lake Linden and Tamarack divisions of the Calumet and Hecla Consolidated Copper Company are the only hydrometallurgical installations in operation at present which utilize an ammoniacal leach. The ammoniacal leaching process was originally adopted in 1916 for the recovery of native copper from conglomerate and amygdaloid tailings, which are too low in copper content to be economically treated in any other way. Evidence of the success of the operations can be measured by the data which follow:

1916-1951	Lake Linden	Tamarack
Tons treated	37,912,800	16,888,220
Per cent copper, heads	0.686	0.466
Per cent copper, tails	0.127	0.100
Pounds of copper recovered	422,986,479	112,174,179
Pounds per ton extracted	11.6	7.23

In the treatment of ore or tailings the coarser native copper is recovered by gravity concentration, followed by the classification and separation of plus 100-mesh sands for the ammoniacal leach. Minus 100-mesh sands are treated by flotation methods for the recovery of the contained copper. The plus 100-mesh tails, averaging less than 0.7 per cent copper, represent approximately 10 per cent of the original feed. The chemistry of the dissolution and subsequent recovery of the contained copper as copper oxide have been discussed. The leaching method used is batch, downward percolation. Steel leaching tanks of 1,000-ton capacity are equipped with water-seal covers (to prevent loss of NH_3), filter bottoms of cocoa matting, and central-cone discharges. Loss of chemical solvent is compensated for by the addition of purchased ammonia and CO_2 to the system. CO_2 is made by burning coke in a Holland furnace and leading the exhaust gases along with air to the oxidizing towers, where cupric ammonium carbonate is regenerated for leaching purposes through the oxidation of the cuprous ammonium carbonate formed in the leaching cycle. Cupric ammonium carbonate is the active leaching agent.

The leaching of copper from secondary materials was tried on a small scale in 1937 and has gradually been increased so that at present only a minimum amount of current tailing is being treated. In a normal scrap market, substantial quantities of scrap copper are treated both on a purchase and toll basis. Since iron and steel do not dissolve in the leaching solutions, bimetallic scrap is an ideal material for the process. Recovery of both copper and iron is effected.

Rio Tinto[34]

Hydrometallurgical treatment for the recovery of copper from low-grade massive pyrites has been practiced in Spain for centuries. The method used most extensively has been heap leaching, followed by chemical precipitation with iron. Recent changes, in the basically unchanged process, have centered largely around attempts to build more uniform heaps and thus to provide better access of air for oxidation of the sulfide copper to water-soluble sulfate. The temperature gradient of the heap has been found to be an important consideration in the efficiency of the leach. The addition of leach solutions, by sprays, is now regulated to maintain a nearly uniform temperature of about 70°C in the heap.

The ore is now running about 1.5 per cent copper, of which from 75 to 85 per cent is recovered in a two-year cyclic leach. The rate of recovery is about 100 grams of copper per month per ton of original ore. The final gangue assays about 0.3 per cent copper. Leaching beyond this point has been found to be a marginal consideration.

To conserve iron in the cementation circuit, all leach liquors are treated with SO_2 gas to reduce contained ferric iron to ferrous iron. Approximately 1.44 tons of metallic iron or 1.56 tons of 90 per cent iron content scrap are required per ton of cement copper produced.

Union Minière du Haut Katanga[35]

The hydrometallurgical division of Union Minière du Haut Katanga at Jadotville-Shituru, Belgian Congo, is now confined to the treatment of flotation concentrates made from the oxide ores. The ore minerals are malachite, chrysocolla, and pseudo-malachite associated in a highly altered gangue of argillaceous or siliceous schists.

The concentrates (± 28 per cent copper) contain quantities of primary slimes of more or less colloidal character and are thus not amenable to the more conventional percolation leach. A continuous suspension leach, utilizing pneumatic agitation of the Pachuca type, has given satisfactory dissolution of the copper minerals with dilute sulfuric acid. After clarification and washing of the leach pulp, a final filtration is still necessary for satisfactory electrolysis of the pregnant solution. Filtration is effected through filter beds, which are formed of layers of gravel. Other methods tried have been fruitless.

Ferric iron content of the electrolyte is controlled previous to electrolysis by neutralizing part of the leach solution with copper ores of basic character. The presence of phosphoric acid makes possible the precipitation of the ferric iron as ferric phosphate. The rest of the electrolytic treatment is typical with possibly one exception. Electrolytic cells are 65½ feet long and contain 191 anodes and 188 cathodes per cell.

The plant is presently being enlarged for an anticipated 100,000-ton annual production.

Nchanga Consolidated Copper Mines, Ltd.[36]

Smelting of mixed oxide-sulfide concentrates at the Nkana smelter of the Nchanga Consolidated Copper Mines, Ltd., Northern Rhodesia, posed problems, in that excessive amounts of limerock as well as an extraneous supply of iron and sulfur were necessary. The recovery of the oxide copper by leaching resulted in a satisfactory economic solution to an otherwise costly problem.

At present a high-grade sulfide concentrate (smelted) and a lower-grade oxide concentrate are being made. In the recently completed leaching division, the oxide concentrate is leached with dilute sulfuric acid in an agitation-type circuit, the pulp clarified and washed by conventional methods, and the copper contained in the resultant leach solutions recovered electrolytically.

OTHER HYDROMETALLURGICAL PROJECTS

Among new leaching projects which are either under construction or under consideration at present are the following: Copper Range Company, in Michigan; Anaconda Copper Mining Company, in Nevada; North Butte Mining Company, in Montana; Sherritt Gordon Mines, Ltd., in Canada; and Tsumeb Corporation, Ltd., in South Africa. As proposed, all would be in production by 1954.

Several other hydrometallurgical projects were operated successfully for a number of years, but because of exhausted resources are no longer in operation. Among these the Kennecott, Alaska, operations of the Kennecott Copper Corporation and the activities of the Ohio Copper Company have been mentioned. Two others worthy of mention are the Ajo, Arizona, operations of the New Cornelia Copper Company, and the South African operations of Bwana M'Kubwa Company.

In the period from 1917 to 1930, New Cornelia treated approximately 17,000,000 tons of low-grade ore[37]. Sulfuric acid, with such ferric sulfate as was inherent in the process, was used in an 8-day, countercurrent, upward percolation leaching cycle. SO_2 gas was used to reduce ferric iron in the leach liquors previous to the electrolytic precipitation of the contained copper. Bleeding electrolyte and chemical stripping, using scrap iron as the precipitant, controlled other impurities.

The novel feature of the Bwana M'Kubwa process was the prior heat treating and subsequent reduction of the ore with producer gas. The reduction reaction was very rapid, taking place in about 20 minutes, under carefully controlled conditions. The reduced copper was then leached with cupric ammonium carbonate in a process very similar to that of Calumet & Hecla.

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Chapter 14

Commercial Forms of Copper Products

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The definitions of terms used in this chapter correspond closely to those given in the Tentative Classification of Coppers of the American Society for Testing Materials, A.S.T.M. Designation B 224-48 T.

Copper products are generally divided into two classes:

(I) Copper, *i.e.*, metal containing less than 0.5 per cent of alloying elements.

(II) Copper-base Alloys, containing at least 40 per cent copper.

COPPER

Before the various types of copper available in refinery shapes and wrought products are classified, the following definitions should be noted:

Terms Relating to the Method of Refining

Electrolytic Copper. Copper which has been refined by electrolytic deposition, including cathodes, which are the direct product of refining operations; refinery shapes cast from melted cathodes; and, by extension, products of fabricating plants made from such shapes. When the term electrolytic copper is used alone, it usually refers to electrolytic tough-pitch copper without elements other than oxygen being present in significant amounts. The copper must have a minimum purity of not less than 99.90 per cent, silver being counted as copper.

Fire-refined Copper. Copper which has been refined by a furnace process only. The term includes refinery shapes, and, by extension, products of fabricating plants made therefrom. When this term is used alone, it usually refers to fire-refined tough-pitch copper containing no elements other than oxygen in significant amounts. The copper plus silver must not be less than 99.70 per cent.

Lake Copper. This term is applied to copper which is produced from ore mined, smelted, and refined in the northern peninsula of Michigan.

There are two grades: (a) low-resistance, having a purity of 99.900 per cent copper and low resistivity, *i.e.*, corresponding to that of electrolytic copper; and (b) high-resistance, having a purity of 99.900 per cent, silver and arsenic being counted as copper. The resistivity of this copper is greater than 0.15694 ohms per meter-gram.

Lake copper may be refined either electrolytically or by furnace process only, *i.e.*, by fire refining.

Terms Relating to Characteristics Determined by the Method of Casting or Processing

Tough-pitch Copper. Copper refined either electrolytically or fire-refined which has been cast in the form of refinery shapes containing a controlled amount of oxygen in order to obtain a level set on the surface of the casting. By extension, this term is also applicable to fabricators' products made therefrom.

Oxygen-free Copper. Electrolytic copper free from cuprous oxide, which has been produced without the use of residual metallic or metalloidal deoxidizers[1]. By extension, the term is also applicable to fabricators' products made therefrom[2]. (Note: This type of copper is free from cuprous oxide as determined by microscopic examination at a magnification of 75x).

Deoxidized Copper. Copper cast in the form of refinery shapes, which has been made free from cuprous oxide by use of metallic or metalloid deoxidizers. By extension, the term is also applicable to fabricators' products made therefrom.

Terms Relating to Specific Kinds of Coppers

High-conductivity Copper. Copper which, in the annealed condition, has a minimum electrical conductivity of 100 per cent I.A.C.S. (International Annealed Copper Standard) as determined in accordance with A.S.T.M. methods of test.

Casting Copper. Fire-refined tough-pitch copper usually cast from melted secondary metal into ingot and ingot bars only, and used for making foundry castings, but not wrought products.

Phosphorized Copper. A general term applied to copper deoxidized with phosphorus. The most commonly used deoxidized copper.

High Residual Phosphorus Copper. Deoxidized copper with residual phosphorus present in amounts (usually 0.013 to 0.040 per cent) generally sufficient to decrease appreciably the conductivity of the copper.

Low Residual Phosphorus Copper. Deoxidized copper with residual phosphorus present in amounts (usually 0.004 to 0.012 per cent) generally too small to decrease appreciably the conductivity of the copper.

Arsenical Copper, Selenium-bearing Copper, Silver-bearing Copper, Tellurium-bearing Copper. Copper containing the designated element in amounts as agreed upon between the supplier and the consumer. Any of these alloyed coppers can be produced as tough-pitch, oxygen-free, or deoxidized varieties. For the ones commonly supplied see Table 14-1.

Shapes Produced by the Copper Refineries

In a previous chapter it was pointed out that the end product of the electrolysis, the cathode, is a flat plate of copper, which is usually about 3 by 3 feet and about ½ to ⅞ inch thick and weighs up to about 280 pounds. The copper, composed of elongated crystals, while tough and hard, is not suitable for fabricating into commercial products such as rod, wire, sheet, tube, etc. It is, however, ideal for melting into the shapes

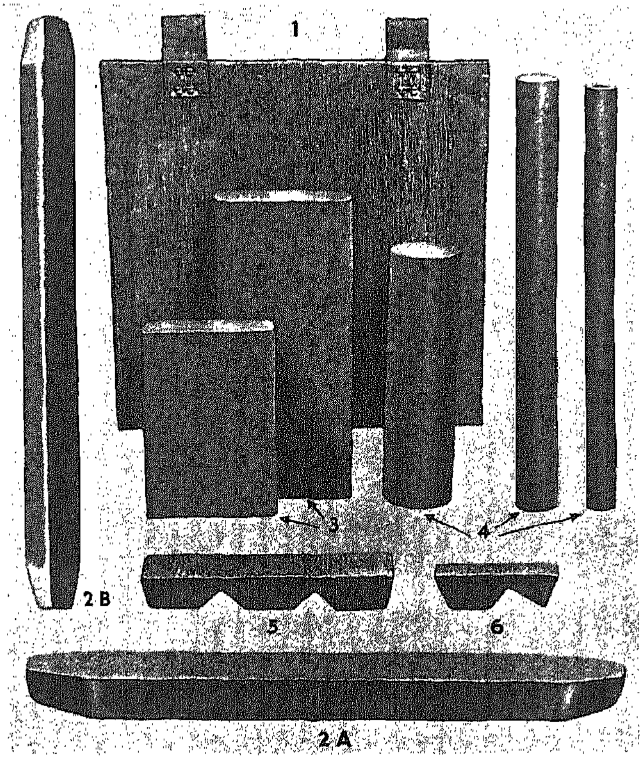

FIGURE 14-1. Commercial shapes of copper. (Approximately one-sixteenth actual size). (1) Cathode. (2A) Horizontally cast tough-pitch wirebar. (2B) Vertically cast oxygen-free high-conductivity wirebar. (3) Vertically cast cakes. (4) Billets. (5) Ingot bar. (6) Ingot.

customarily produced by the refineries, such as wirebars, cakes, billets, and ingots and ingot bars. A description of these various shapes follows:

Wirebars. These are bars approximately 3½ to 5 inches square in cross section, usually 38 to 54 inches in length, and weigh from 135 to 420 pounds. They are tapered or pointed at both ends when used for rolling into rod for subsequent drawing into wire and may be unpointed when used for rolling into strip. Wirebars are usually cast horizontally in open tray molds or vertically in water-cooled static molds or in continuous casting machines. A number of refineries furnish "scalped" wirebars. These are horizontally cast tough-pitch wirebars of which the set surface, consisting largely of cuprous oxide, has been removed by scalping or planing.

*Cakes**. These are rectangular shapes used for rolling into plate, sheet, strip, or other shapes. They are cast either horizontally in open tray molds or in water-cooled vertical molds. They range in weight from 140 to about 4,000 pounds.

*Billets**. These are circular in cross section, usually 3 to 10 inches in diameter and up to 52 inches in length. The weight ranges from about 100 to 1,500 pounds. Billets are used for manufacture of tubes either by piercing or extrusion.

Ingots and Ingot Bars. These shapes are used primarily for remelting and subsequent production of copper and copper-alloy castings; they are not used for direct fabrication. Ingots, cast in open tray molds, usually weigh from 20 to 35 pounds, ingot bars from 50 to 70 pounds. Both are usually notched to facilitate breaking into smaller pieces.

FABRICATORS' COPPER PRODUCTS

Reference has been made in the previous paragraph to the principal products fabricated from the shapes supplied by the refineries. A description of these products follows:

Wire. This product, which is defined in A.S.T.M. Classification of Coppers (B 224-48 T) as "a solid section, other than strip, furnished in coils or on spools, reels or bucks," is nearly always made by hot rolling wirebars into rod and then drawing the rod into wire. Most wire is circular in cross section, but for special purposes it is often furnished with other cross sections. It can be supplied in various tempers; also plain, tinned, enameled, or insulated; and as a single wire or stranded. Sizes range from about ½ inch in diameter down to 44 AWG (American wire gage), or 0.001978 inch in diameter. As copper wire is usually employed for conducting electricity, it must be made of a type of copper having high electrical conductivity.

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* Cakes and billets are also produced by continuous casting processes.

Tube. This product is described in the A.S.T.M. Classification as "a hollow product of round or any other cross section, having a continuous periphery." Tubing, as it is often called, is supplied in straight lengths or in coils, and in various tempers. The A.S.T.M. makes a distinction between tube and pipe, defining the latter as follows: "Seamless tube conforming to the particular dimensions commercially known as "Standard Pipe Sizes."

Flat Product. This is defined as "a rectangular or square solid section of relatively great length in proportion to the thickness." Plate, sheet, strip, and bar are included in the designation "Flat Product." Certain sizes of flat wire are also included in this designation.

Shape. This is defined as follows: "A solid section, other than rectangular, square, or standard rod or wire sections, furnished in straight lengths." Shapes are usually made by extrusion but sometimes by hot rolling followed by drawing.

Rod. Most rod is made by hot rolling and is usually circular in cross section. Large-diameter rod, that is ⅞-inch diameter and over, is usually made by extrusion. Round rod for further processing into wire is furnished in coils. Rod for other purposes, usually in hard temper, is furnished in straight lengths. Some hexagonal and octagonal rod is also produced.

CLASSIFICATION OF COPPERS

After studying this subject for a number of years, a joint committee of the American Society for Testing Materials representing prime producers and fabricators prepared a classification of coppers which bears the designation Tentative Classification of Coppers B 224-48 T. Table I of this classification is reproduced herewith as Table 14-1.

SPECIFICATIONS

Throughout the United States copper is almost always sold in accordance with the specifications of the American Society for Testing Materials. This society, now over 50 years old, is sufficiently well known throughout the technical world not to require description. Its standing is of the highest order and the specifications issued by it are universally accepted by buyers and sellers.

Copper in cast form is sold according to the following six A.S.T.M. specifications:

(1) B 4-42:	Covering Lake copper, wirebars, cakes, slabs, billets, ingots, and ingot bars.
(2) B 5-43:	Covering electrolytic copper wirebars, cakes, slabs, billets, ingots, and ingot bars.

TABLE 14-1. CLASSIFICATION OF COPPERS

Designation	Type of Copper	Forms in Which Available[a]							
		From Refiners				From Fabricators			
		Wire-bars	Bill-ets	Cakes	Ingots and Ingot Bars	Flat Prod-ucts	Pipe and Tube	Rod and Wire	Shapes
CATH	Electrolytic cathode	Available in cathodes only				......	......	......	......
	TOUGH-PITCH COPPERS								
ETP	Electrolytic tough-pitch[b]	X	X	X	X	X	X	X	X
FRHC	Fire-refined high-conductivity tough-pitch[b]	X	X	X	X	X	X	X	X
FRTP	Fire-refined tough-pitch	......	X	X	X	X	X	......	X
ATP	Arsenical, tough-pitch	......	X	X	......	X	X	X	......
STP	Silver-bearing tough-pitch[b]	X	X	X	X	X	X	X	X
SATP	Silver-bearing arsenical, tough-pitch	......	X	X	......	X	X	......	......
SETP	Selenium-bearing, tough-pitch	......	......	......	......	......	......	X	X
TETP	Tellurium-bearing, tough-pitch	......	......	......	......	......	......	......	X
CAST	Casting	......	......	......	X	......	......	......	......
	OXYGEN-FREE COPPERS								
OF	Oxygen-free without residual deoxidants[b]	X	X	X	d	X	X	X	X
OFS	Oxygen-free, silver-bearing[b]	X	X	X	......	X	......	X	X
OFTE	Oxygen-free, tellurium-bearing	......	......	......	......	X	......	X	X
	DEOXIDIZED COPPERS								
DHP	Phosphorized, high residual phosphorus	X	X	X	......	X	X	X	X
DLP	Phosphorized, low residual phosphorus[c]	......	X	X	......	X	X	......	X
DPS	Phosphorized, silver-bearing	......	X	X	......	X	X	......	X
DPA	Phosphorized, arsenical	......	X	......	......	X	X	......	......
DPTE	Phosphorized, tellurium-bearing	......	......	......	......	......	......	X	X

[a] *The X in the table indicates commercial availability.*

[b] Types ETP, FRHC, STP, OF, and OFS are high-conductivity coppers.

[c] Type DLP can be *furnished as a high-conductivity copper if agreed upon between the supplier and the purchaser.*

[d] Croppings of other shapes available and can be used as ingots.

(3) B 72-47 T:	Covering fire-refined casting copper.
(4) B 115-43:	Electrolytic cathode copper.
(5) B 170-47:	Oxygen-free electrolytic copper wirebars, billets, and cakes.
(6) B 216-49:	Fire-refined copper for wrought products and alloys.

Specifications B 4-42 and B 5-43 have been approved as American Standard by the American Standards Association. Specification B 72-47 T is Tentative; all the others are Standard.

The American Society for Testing Materials publishes, besides its regular volumes of specifications, a special volume containing only the A.S.T.M. Standards on Copper and Copper Alloys. This excellent volume, revised every two years, should be consulted by all who manufacture, sell, or buy copper in any form.

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Chapter 15

Copper and Copper-Base Powders

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During the past twenty-five years or so, the use of many and varied parts made from metal powders has grown by leaps and bounds. The products of the powder-metallurgy process have found wide usage as machine components. This unique process is now given equal consideration with conventional fabricating techniques by engineers who design and build automotive, railroad, farm, aircraft, marine, and communications equipment, as well as such everyday household appliances as washers, dryers, ironers, electric fans, refrigerators, etc.

Metal powders of single elements, or in combination with other metals or nonmetals, are compressed, sintered, and sized to exacting tolerances in the manufacture of oil-impregnated porous bearings, cams, gears, magnets, carbide cutting tools, motor brushes, clutch facings, contact points, grinding wheels, filters, filaments, lock assemblies, plus many parts of various shapes far too numerous to mention here.

Many different kinds of metal powders are now commercially produced and utilized by industries in improving their products and lowering production costs. These include tungsten, molybdenum, zirconium, silver, platinum, iron, nickel, cobalt, copper, tin, lead, aluminum, etc., plus various alloy powders such as solders, brasses, bronzes, copper-leads, etc.

The reasons for the rather phenomenal growth of the powder metallurgy industry in the recent past where the number of pieces required is high are simple and few, and may be summed up as follows:

(1) Ability to achieve properties unobtainable by conventional methods (controlled porosity, nonequilibrium alloys, metal-nonmetal combinations, cemented carbides, etc.)

(2) Lower labor costs due to elimination of machining operations plus complete utilization of raw materials.

(3) Adaptability to mass-production techniques of flexible, multipurpose equipment (completely automatic presses and furnaces utilized for a wide variety of parts.)

(4) Elimination of assembly operations because of unique design factors permissible in powder-metallurgy parts.

Most metal powders are commercially produced by electrolysis, gaseous reduction of oxides, or atomization. Less widely used methods include precipitation, carbonyl decomposition, and comminution of solids.

Metal powders to be suitable for the fabrication of sintered parts must meet exacting physical and chemical requirements. The more important of these are as follows:

(1) Purity: Elements which tend to decrease the inherent ductility or seriously impede diffusion cannot be tolerated.

(2) Flow: Free-flowing characteristics are essential to permit automatic and uniform feeding of die cavities.

(3) Compactibility: Powders must compact to strong enough bodies of the required green strength and density to permit handling prior to the sintering or heat-treating operation.

(4) Sintering characteristics: When metal powder compacts are sintered, either in the solid state or in the presence of a minor portion of a liquid phase, suitable physical and mechanical properties must be obtained within predictable and reproducible dimensions.

Some of the powder characteristics controlling these properties such as purity, particle shape, particle hardness, particle porosity, and particle surface reflect the method of powder manufacture. Other characteristics which may be varied within rather wide limits in most of the manufacturing processes include apparent density, particle-size distribution, and oxide content. The variety of particle shapes obtained in different methods of making copper and copper-alloy powders is illustrated in Figure 15-1.

Methods of Testing

The powder-metallurgy industry generally uses the following test procedures for determining the characteristics of metal powders.

Sampling. The most important part of any evaluation test is the obtaining of a representative sample. This is particularly true of finely divided materials. Containers of powders which have not been thoroughly blended are usually sampled by forcing a hollow pipe, called a "thief," vertically to the bottom of the container and removing a column of powder. One or more of these columns are removed from the container depending upon its size and shape. Samples taken in this manner are combined and reduced to required size by splitting. Rolling and coning are sometimes substituted for splitting.

Particle-size Distribution. A complete determination of particle-size distribution of a powder is obtained by first determining its screen analysis. A weighed sample of powder is placed in the top screen of a

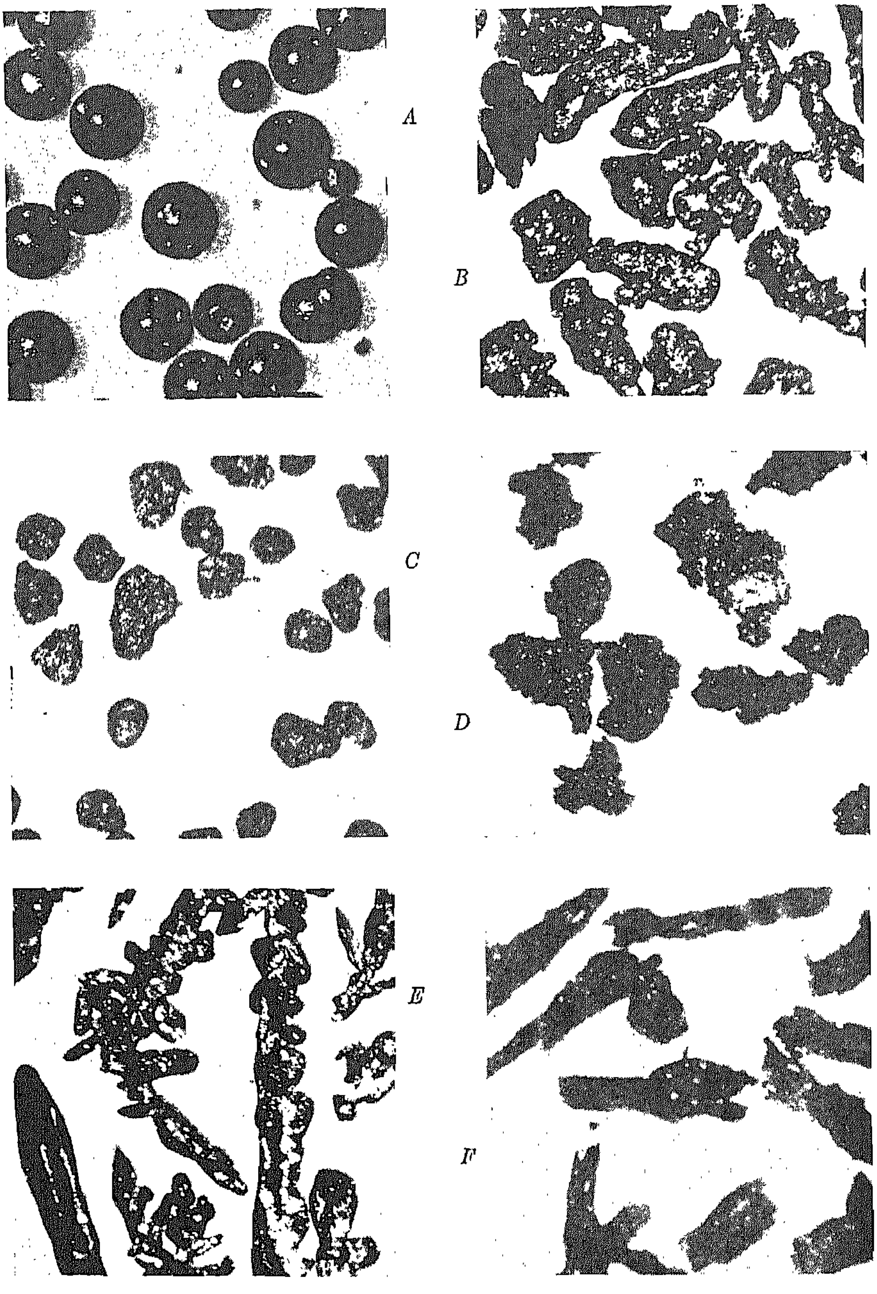

FIGURE 15-1. Photomicrographs of different particle shapes produced in copper and copper-alloy powders. Magnification 75X. (*a*) Spherical. (*b*) Irregular. (*c*) Globular. (*d*) Porous. (*e*) Dendritic. (*f*) Acicular.

nest of standard sieves having successively smaller openings (usually 100, 150, 200, 250, and 325 mesh) and mechanically shaken in a "Rotap" for a standard time interval. The fractions retained on each mesh size and the entire portion passing the finest sieve are reported as a weight percentage of the whole sample. The minus 325-mesh fraction is frequently further analyzed for subsieve size distribution by means of the microscope, roller air analyzer, Wagner Turbidimeter, Fisher Subsieve Sizer, or other types of apparatus, and the results are reported for decreasing micron size ranges as weight percentages of the whole sample.

Flow Rate. This test is usually performed with a standard Hall flowmeter, which is a funnel-shaped apparatus having a calibrated orifice. The time required for a given amount of powder to flow unaided through the orifice is the value reported as flow rate.

Apparent Density. The standard flowmeter is used for free-flowing powders. For nonflowing powders, use is made of the Scott Volumeter, an instrument consisting of a baffled, rectangular tower fed by a funnel having a large orifice. Both serve to supply a controlled flow of powder into a cup of known volume. The contents of the leveled, full cup is weighed and the apparent density reported as grams per cubic centimeter.

Weight Loss in Hydrogen. A fairly accurate indication of the oxide content of most metal powders is determined on a weighed sample under standard time-temperature conditions. Heat treatment and subsequent cooling to room temperature must be conducted in an atmosphere of dry hydrogen.

"Loss in hydrogen" is expressed as a percentage of the initial weight.

Compressibility. As an indication of pressing characteristics, this test is performed by compacting a given weight of powder at a definite pressure in the test die under controlled standard conditions. The ratio of the apparent density of the compact to the theoretical density of the component metals is a measure of powder compressibility.

Green Strength. The strength of a compacted but unsintered specimen is ordinarily determined by pressing a given weight of powder to a specified density in the shape of a rectangular bar of standard size. The test bar is subjected to transverse loading as a simple beam supported at both ends. The modulus of rupture in pounds per square inch is reported as green strength.

Sintering Characteristics. To determine these characteristics a weighed quantity of a standard powder mixture is compacted under controlled conditions and the dimensions of the specimen recorded. After sintering, the specimen is again weighed and measured. It is then tested to fracture for strength. The sintering characteristics are generally reported in terms of dimensional and density changes, final density, strength, and ductility.

In addition to the above tests, many others may be used to determine the physical and mechanical properties of a sintered compact.

PRODUCTION METHODS FOR COPPER AND COPPER-BASE ALLOY POWDERS

Relatively few processes are suitable for the commercial production of metal powders for powder-metallurgy purposes because of the narrow limits of the many specifications imposed. In the copper and copper-base alloy fields, the following methods have become firmly established. These processes are listed in the general order of their respective contribution to the total present production.

(1) Electrolytic deposition in copper sulfate solutions using soluble anodes.

(2) Gaseous reduction of finely divided oxides.

(3) High-velocity atomization of molten copper or alloys by compressed gas, steam, or a stream of water.

(4) Precipitation from solutions.

Electrolytic Copper Powder

Most electrolytic copper powders are produced by electrodeposition using a soluble anode and a cathode which is chemically inert to the electrolyte. In commercial practice the main purpose of the electrolytic step is to transform solid copper into discrete, finely divided particles whose characteristics can be controlled and reproduced. Uniformity of product is extremely important. Slight variations in the processing conditions may alter the end product sufficiently to render the material unsuitable for the application intended.

Since high purity is essential, the starting material used for anodes is refinery cathode copper.

Large-scale attempts to use copper of lower purity as the starting material, with the intention of including refining as well as powder formation in the electrolytic step, have not been fruitful because of the wide variations in the chemical and physical characteristics of the end product. Electrolytic processes have been investigated utilizing insoluble anodes, but have not proved commercially feasible for the production of high-grade copper powders.

The most suitable material found thus far for use as cathodes is lead alloy sheet. Because of the severe electrochemical conditions prevailing in the cells, other materials such as silicon-iron, briquetted iron oxide, stainless steel, and graphite, to name a few, have not proved successful in comparison with lead-base cathodes.

The electrodes are arranged in parallel in lead-lined or rubber-lined tanks, and are frequently inspected for irregularities to insure uniform current density and elimination of short circuits in the cells.

In contrast to the normal electrolytic copper refining practice, electrolysis for the production of powder is carried on at a much higher current density, and requires closer control of electrolyte temperature, composition, and circulation.

By suitable control at various levels within this narrow range, marketable copper powder is produced varying from 1.5 to 3.5 grams per cubic centimeter in apparent density and from 30 to 98 per cent minus 325-mesh in particle size. It is necessary to produce powders having such a wide spread in physical characteristics because of the widely differing demands of the industry.

During electrolysis, copper deposits as discrete particles at the cathode and is collected in this form at the bottom of the cell. Periodically this sludge is removed and washed free of electrolyte. The handling of the powder after removal from the tanks is critical because of the tremendous surface area and activity of wet copper powder. Thorough washing and immediate drying are essential to prevent excessive oxidation of the material while in this state.

The powder is dried in conventional controlled-atmosphere furnaces of the continuous type. Reducing rather than neutral conditions are maintained to remove any surface oxides which may have formed during and after washing. Depending upon the type of powder being treated the furnaces are operated at temperatures of from 315 to 760°C (600 to 1400°F) and the furnace atmospheres may contain from 10 to 30 per cent hydrogen plus 5 to 20 per cent carbon monoxide. Furnace conditions for any particular type of powder are very closely controlled. The main difficulty in drying is the prevention of excessive fritting or sintering of the powder into a ductile mass which cannot be broken down again to a suitable end product.

The discharge from the furnaces is fed to high-velocity impact mills to restore the original mesh size of the powder without excessively cold working and thus hardening the particles. The speed and rate of feed to the mills are controlled within close limits, for powder which is milled too lightly will contain a high percentage of agglomerated fines and powder which is milled too heavily will contain flakes, roughly spherical, or cold-worked particles which will destroy its compacting qualities. Between these two extremes a balance is maintained to produce unit particles having the desired characteristics.

The powder is then fractionated by screening and air separation. The various fractions are collected, a representative sample sent to the control laboratory and the material stored in airtight, dessicated containers. The control samples are analyzed and the chemical and physical characteristics tabulated.

The final production step involves blending of the various fractions to produce the desired type of powder. A careful selection of material is made based on experience and on the tabulated characteristics of the stock metal. These fractions are fed into a conical blender and mixed until the entire charge is uniform in all respects. A representative sample of the blend is checked in the control laboratory and if the required properties are obtained the powder is then packed in hermetically sealed steel drums containing a dessicant.

Reduced Copper Powder

In the production of copper powder by gaseous reduction, the raw materials include various types of relatively high-grade scrap, mixed oxides, plus ingot metal of both primary and secondary grades. Depending upon the purity and form of the starting material, one or more of the following steps may be necessary in the preliminary operations:

(1) Smelting and refining of impure metal.

(2) Transformation to a globular, granular, or flake form by shotting, atomizing, shaving, or shredding.

(3) Conversion to oxide by roasting.

In the form of oxide, the material is very friable and is comminuted to a fine powder by conventional milling methods. This operation must be carefully controlled because variations in the particle-size distribution of the copper oxide itself will strongly influence the characteristics of the final product.

The gaseous reduction step is performed in controlled-atmosphere continuous furnaces at temperatures of 480 to 870°C (900 to 1600°F) depending upon the type of powder required. A rapid flow of reducing atmosphere, usually containing more than 50 per cent hydrogen and carbon monoxide, is maintained through the furnace to promote the most favorable conditions for oxide decomposition. The furnace product is a fritted copper cake which must be broken up and milled to a powder.

The final operations such as milling, sizing, blending, control testing, and packing are in general similar to those described for the electrolytic process. The physical characteristics of reduced powders approach those of electrolytic and many fabricators of parts use both types.

The production and properties of copper powder prepared by reduction of copper oxide have been studied by Ellwood and Weddle[1]. Their paper compares the properties of powders of different size distribution, made both by reduction with hydrogen and with carbon monoxide, with powders produced by electrolysis and by atomization with steam. Since high tensile strength was obtained in sintering without appreciable decrease in hardness, it is indicated that pronounced sintering is possible at temperatures below the recrystallization temperature.

Atomized Copper and Alloy Powders

By subjecting a thin stream of molten metal to the violent disintegrating and quenching action of a high-velocity jet of water, steam, air, or gas of special composition, a wide range of copper and copper-base alloys are commercially produced as "atomized" powders. These include straight brasses and bronzes, copper-lead "alloys," leaded brasses and bronzes, plus various special alloys. By suitable control of the temperature, composition of the melt, type of atomizing fluid, and choice of cooling medium, this process can be used to produce powders of irregular, globular, or spherical particle shapes.

In the straight brasses and many of the other alloys, the particles are characterized by heavily cored dendritic structures. These appear to promote better sintering than do equilibrium structures, possibly through the medium of a higher diffusion gradient. In contrast, copper-lead powder particles contain finely dispersed lead islands in a matrix of copper.

While several variations are practiced in industry, the general steps in production consist of melting and heating the metal or alloy from one hundred to several hundred degrees Fahrenheit above its melting point under a solid or gaseous protective cover and then passing it through a suitable orifice to form a thin stream. The atomizing nozzle is located so as to permit the high-velocity fluid to travel in a plane approximately normal to the axis of the stream of metal. The atomizing chamber is of such shape that the disintegrated metal solidifies and cools before impinging on any surface. This prevents the building up of accretions.

The particle-size distribution of atomized powders is controlled by the temperature of the molten metal, size of the molten stream, and pressure of the atomizing medium.

Where a liquid medium is used for atomization, the wet powder is dewatered by settling or filtering and dried in a protective atmosphere.

The remaining steps in the process from screening through packing follow the same general pattern described under electrolytic copper powder.

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Chapter 16

Secondary Copper and Copper Alloys

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In the proportions to which it has grown since the First World War, the secondary copper and copper-base alloy industry is a vital factor in the structure of nonferrous metal production. The growing pains suffered by the secondary nonferrous industry prior to 1914 were acute. The strides made from that time to the present have overcome the early handicaps imposed by erroneous economic and technical considerations. The percentage of the total national output of copper and its alloys supplied by the secondary industry has reached a point which indicates that it would be impossible for producers of primary metal to meet the country's requirements without the secondary production.

Importance of Secondary Copper

During the five-year period 1948-1952 the consumption of primary copper in the United States averaged 1,313,000 short tons annually. In the same period the tonnage of copper recovered from old scrap averaged 452,000 tons annually, and the total secondary copper recovered including that contained in alloys but not separated therefrom in treatment averaged 903,000 tons annually. The latter figure is significant because it represents the total requirement of copper that would have to be supplied from primary production in addition to actual primary output if no recovery of scrap material were made. This total of secondary copper averaged 104 per cent of the United States mine production of copper during this period*.

Table 16-1 gives the breakdown of the total secondary copper recovery into that produced as unalloyed copper and that recovered as copper contained in alloys; also, the amount recovered from new scrap (*i.e.*, scrap resulting from manufacturing) and old scrap. These figures include the copper contained in scrap alloys other than copper-base (*viz.*, alloy iron and steel, and aluminum, nickel, lead, tin, and zinc alloys containing minor amounts of copper); also copper contained in secondary chemical compounds. However, about 95 per cent of all the secondary copper recovered in these products is contained in brass and bronze.

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* The figures cited are those published by the U. S. Bureau of Mines and the American Bureau of Metal Statistics.

TABLE 16-1. SECONDARY COPPER PRODUCED IN THE UNITED STATES[a]
(In tons of 2,000 pounds)

	1948	1949	1950	1951	1952
As unalloyed copper	284,026	250,089	260,704	186,462	182,000
Recovered in alloys*	688,762	463,054	716,535	745,820	740,000
Total secondary copper	972,788	713,143	977,239	932,282	922,000
From new scrap	467,324	329,595	492,028	474,158	492,000
From old scrap	505,464	383,548	485,211	458,124	430,000

* Includes some copper contained in chemical products; these amounts are shown in Table 16-2.
[a] U. S. Bureau of Mines.

In Table 16-2 there is shown the distribution of the secondary copper production according to the type or form of copper or copper-alloy product.

TABLE 16-2. PRODUCTION OF SECONDARY COPPER AND COPPER PRODUCTS[a]
(In tons of 2,000 pounds)

	1949	1950	1951
Unalloyed copper	250,089	260,704	186,462
Total weight of brass and bronze ingots, all compositions	200,046	340,687	365,754
Brass-mill billets by ingot makers	2,641	2,828	5,786
Wrought brass and bronze products	265,439	418,598	424,077
Brass and bronze castings	99,419	131,936	137,895
Brass powder	886	906	1,171
Copper in chemical products	14,840	17,413	22,905
Totals	833,360	1,173,072	1,144,050

[a] U. S. Bureau of Mines.

The data in Tables 16-1 and 16-2 indicate clearly the magnitude of the secondary metal industry. Scrap is the life blood of this industry. The U. S. Bureau of Mines reports that in 1949 a total of 1,096,138 tons of scrap of all kinds was used in the United States, and 1,441,172 tons in 1950. The secondary ingot producers achieve an over-all recovery of about 85 per cent (including residues and low-grade stocks).

Classes of Scrap

At one time there were more than 600 copper-base alloys in use in American foundries. There was an acute need for simplification and standardization. In 1938, *The Metal Industry* presented a classification system in its "Casting Manual for Non-ferrous Metals" which was subsequently studied, revised, and adopted by the American Society for Testing Materials. This system has been tentatively approved by the Brass and Bronze Ingot Institute and recommended for use by the foundry industry. The system is based upon the use of the term "bronze" to designate copper-base alloys of 98 per cent maximum copper, containing elements other than zinc. Zinc may be present, but only in concentrations which keep the effect of zinc on physical properties subordinate to the effect of the other elements. "Brass" designates a copper-base alloy with zinc containing not over 98 per cent copper. Other elements may be present but only in such concentrations that their effect on the physical properties of the alloy will be subordinate to the effect of the zinc. Alloys of more than 98 per cent copper are classed as copper. The final system was composed of twenty-three groups of cast copper-base alloys, which include virtually all of the standard compositions in present use.

The grades of scrap encountered in the secondary field originate from these groups. Most metal dealers and supervisors of plant salvage departments take advantage of the economy in using clean segregated scrap. However, thousands of tons of mixed and contaminated scrap material are received by the smelters. The form of the scrap, as well as its composition, is of great interest. Scrap may be "new," such as that produced in manufacturing operations using primary materials. Or it may be "old," such as domestic waste, utensils, or materials from salvage and demolition operations.

Scrap comes in the form of turnings and borings, grindings, clippings, heavy solids, condenser tubing, automobile radiators, and industrial castings. All sizes of wire and cable (with and without insulation) are received. Scrap may be in an infinite variety of stamped and formed shapes from rolled stock. Another important class of material handled in appreciable tonnages includes slags, drosses, skimmings, and concentrates. The metallic content of these latter items may vary from a few per cent to more than 60 per cent. The low metallic content of these materials normally render them unsuitable for direct smelting operations and they are first melted in a cupola for subsequent refining.

Copper and brass scrap classifications which are used in the secondary industry today, and which cover all commercial grades of scrap, are tabulated with definitions in the Office of Price Stabilization schedules. Aside from serving as a pricing basis, the schedule is the yardstick for segregation in smelting operations. The schedule is shown in Table 16-3.

TABLE 16-3. COPPER AND BRASS SCRAP CLASSIFICATION

No. 1 Heavy Copper and No. 1 Copper Wire
No. 2 Copper Wire and Mixed Heavy Copper
Copper Tuyères
Light Copper
No. 1 Copper Borings
No. 2 Copper Borings
Lead-covered Copper Wire and Cable
Refinery Brass
Bell Metal
High-grade Bronze Gears
Tinny Phosphor Bronze Solids and Borings
High-grade Low-lead Bronze Solids and Borings
High-lead Bronze Solids and Borings
Soft Red-brass Solids
Soft Red-brass Borings (No. 1 Composition Borings)
Mixed Brass Borings
Copper-Nickel Solids and Borings
Bronze Paper-mill Wire Cloth
Ford Aluminum Bronze Gears
Aluminum Bronze Solids
Contaminated Gilding-metal Solids and Turnings
Unlined Standard Red Car Boxes
Lined Standard Red Car Boxes
Cocks, Faucets, and Fittings
Mixed Brass Screens
Zincy Bronze Solids and Borings
Red-brass Breakage (Irony Composition)
Automobile Radiators
Nickel-silver Solids and Turnings
Copper-lead Solids and Borings
Heavy Yellow Brass Solids
Yellow Brass Borings
Manganese Bronze Propellers
Manganese Bronze Solids
Manganese Bronze Borings
Fired Rifle Shells
Brass Pipe
Admiralty Condenser Tubes
Muntz-metal Condenser Tubes
Old Rolled Brass
Plated Rolled Brass Sheet, Pipe, and Reflectors

The titles of most of these classifications are self-explanatory. No. 2 copper differs from No. 1 copper essentially in copper content. The minimum copper content of No. 1 is 98.5 per cent and that of No. 2 is 95 per cent. No. 2 copper must be free from other alloys. Copper tuyères are listed separately since they are usually contaminated with iron and scale. Bronze paper-mill wire cloth is listed as a separate item since it is a high-grade composition which is practically free from lead. "Breakage" is used to designate scrap parts and assemblies contaminated with iron, and frequently with other metals, such as brass valves with iron stems, carburetors, etc.

Handling and Treatment of Scrap

A given mass of metal may have gone through the dealer-smelter-foundry-consumer cycle many times. The important fact to note is that with modern handling, segregation, scientifically controlled smelting and refining, the same metal reappears in usable form without deterioration in chemical and physical properties. If desired, copper-base scrap can be refined to high-grade unalloyed copper. The smelter's task is to carry this process to the point of producing whatever alloys he may require.

The first essential in the smelting plant is the most exacting separation practically possible of the scrap into its various classifications. The separation is made on the basis of color, hardness, magnetic properties, type of fabrication, reaction to acids and other reagents, and original source.

The sorting of brass scrap is done piece by piece by highly skilled but nontechnical workmen. A sorter's most valuable tool is a 12-inch rough-cut file which has been magnetized.

In the case of borings, concentrates, punchings, and other reasonably fine material, tramp iron is removed by running the aggregate over a magnetic separator. There are various drum-and-belt types of separators in use. Magnetic separation is an indispensable part of the scrap-preparation procedure.

After scrap has been separated and sorted, each grade is assayed to determine the chemical composition and, in some cases, the metallic content of the material. Assaying involves an actual fire assay of a thoroughly representative portion of a lot, and occasionally an entire batch may be run down in a clean furnace for assay determinations. In the case of large heavy castings, the individual pieces are sampled by drilling or sawing.

The like materials are then stored together and their identifications, metallic content, and composition are entered in the operator's inventory from which he will choose the proper proportions of the various grades to make the alloys required. The metallurgist makes up the furnace charge from available stock on the basis of the greatest economy of material which will insure the required chemical and physical properties in the finished alloy.

The multiplicity of shapes, sizes, and consistency of aggregate scrap poses a serious handling problem in unloading, preparation, and charging. Considerable tonnages must be manually handled as a result of these variances. In conjunction with hand labor, all the various industrial handling techniques are employed.

Fork trucks, high-lift trucks, and car scoops, both electrically and combustion powered, are used wherever practical. Skip hoists, monorail, and bridge cranes are used to great advantage in many operations. Belt and bucket conveyors and, frequently, pneumatic conveyor systems are utilized in the smelting plants. In the plant with which the writer is associated, bridge cranes are used to move and charge material in batches of 10 tons or more.

The handling of special lots of metal often presents individual problems. Progressive operation, however, keeps available all necessary special equipment for speedy material flow at a tolerable cost.

The actual operation of producing a heat of ingot is complex. The method of charging is determined by several factors. The composition of the individual charge, its metallic content, its physical consistency, the type of alloy being made, and the design of the furnace itself impose definite requirements upon the order and method of charging. For example, prefluxed fines contaminated by certain amounts of combustible matter may have to be hand charged, while clean high-metallic fines may be dumped through a hopper by an overhead crane.

In many cases, light, loose, bulky materials such as light brass or loose wire must be briquetted in a press to be conveniently charged and to decrease melting loss. However, the writer is familiar with a furnace, believed to be the largest secondary brass furnace in the industry, which is designed to receive batches of several tons of loose, bulky material in a single charge. In this case, melting and atmospheric controls are employed to provide rapid melting with lowest possible losses.

After the base materials have been charged and melted, the bath is thoroughly mixed with iron rabbles, a sample for chemical analysis is cast, and refining is started. Refining involves fluxing, oxidation, and slagging.

Fluxing consists of the addition of suitable mixtures of limestone, silica, and iron oxides. Mill scale is a common form of iron oxide. Certain other fluxing agents are frequently used for special purposes. Fluxing, in conjunction with oxidation, assists in maintaining suitable slag composition and consistency.

Refining by oxidation consists of the introduction of oxygen into the melt from compressed air, usually through iron pipes. The oxygen reacts preferentially with the impurities to be removed, in the order of their appearance in the electromotive series. As could be expected, however, this reaction is not perfectly selective. As the concentration of an element decreases by conversion to oxide, increasing amounts of the element with the next highest affinity for oxygen are removed.

The existence of such natural physical phenomena in refining imposes conditions which must be carefully controlled throughout the procedure. Practice has been developed through research and experience covering every phase of the process to assure chemical, physical, and quality control. For example, it would be prohibitive practice to remove 30 pounds of iron from a brass heat at the expense of ten times as much zinc which might be removed during the same operation.

Metallurgical control is maintained throughout operation by casting and analyzing samples as frequently as is necessary. An appreciable amount of control must be exercised by the operator at the furnace. In brasses and bronzes it is possible for experienced operators, by visual examination of properly cast samples, to detect less than 0.005 per cent aluminum, silicon, or phosphorus. They can make a reasonable estimation of zinc content in alloys of the red-brass type and can estimate the iron content with an accuracy of plus or minus 0.01 per cent when the iron content is less than 0.25 per cent.

The blowing (oxidation) operation is materially accelerated by maintaining an oxidizing atmosphere during refining. Frequent flux additions are made, principally of silica, to condition the slag. Removals of slag are made as often as necessary. Refining is retarded by heavy slags and also by too much slag even though it is of proper consistency.

Temperature is also an important factor in refining and must be kept in its proper range, which varies with different alloys. In the presence of a ferrous slag at excessive temperature, it becomes exceedingly difficult to take out iron. Under such conditions, however, an addition of silica in conjunction with sudden cooling by a cold charge will cause an immediate drop in iron content of several hundredths of a per cent. The refining of copper-base alloys and the visual control tests are difficult to portray in words. It is a highly skilled procedure and a wealth of experience is required for efficient execution. Operations such as the removal of iron from a high lead-tin bronze without losing tin require exacting control and will be costly indeed if improperly performed.

After refining is completed, the resulting composition will usually require adjustment. Calculated additions of virgin metals are made, bringing the analysis to specification, and the last preliminary chemical and physical tests are made. The heat is tapped and poured into ingots, the final product of the smelter.

Except in the case of exceptionally large heats, bottom taps are made. Pouring is continuous from the taphole, through a launder into a ladle, and then into the ingot molds, made of cast iron. Good ladles are designed to pour from the bottom so that no dross can be washed into the ingot mold. Three to six ingots are poured at a time. Various oil- and water-base mixtures of mold wash are sprayed into the hot molds to prevent sticking of ingots, improve their finish, and increase mold life.

The molds are carried to the ladle on various types of conveyors. The most commonly used are the "buggy" or monorail type, the endless chain, and the turntable or "wheel."

Ingots and molds are water-cooled by passing through spray systems and the ingots are finally dumped automatically into water-filled cooling pits. Endless-chain conveyors lift the ingots out of the cooling pits at a temperature just high enough to deliver them perfectly dry. They are then inspected, properly marked, and are ready for shipment.

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Chapter 17

The Physical Properties of Copper

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Copper is one of the few common metals which find their greatest commercial application in the pure rather than in the alloyed form. This unusual condition is the result of an extraordinary combination of useful properties which make it the basic material of the electrical industry. Naturally, the keystone of this position is its high electrical conductivity, as illustrated in Table 17-1, in which various metals have been compared in terms of relative electrical and thermal conductivity for equal cross sections[1].

While it is apparent why copper initially attained pre-eminence as a material for conductors, the reasons for its ability to hold this position are less obvious and considerably more diverse. Fundamentally this situation is determined by the relative net worth to the consumer of the additional qualifications that copper and its competitive metals can contribute apart from conductivity. The demands of modern industry are so complex that the properties required of a material for conductors may include ease of fabrication, high ductility, reasonable tensile strength, controllable annealing properties, good soldering and joining characteristics, high corrosion resistance, and suitability for electroplating, coating, painting, varnishing, and insulating, not to mention a host of specialized qualifications. Copper possesses these qualities to such a degree that substitution of a competing metal is often possible only when the need for one or more of them can be avoided by the circumstances of the design or application.

As a structural metal, unalloyed copper is used for special properties and functions, but it serves in many instances to great advantage. More often, preference is given to its enormously useful alloys, which furnish the real market for copper in the structural field. In either form, however,

TABLE 17-1. RELATIVE ELECTRICAL AND THERMAL CONDUCTIVITIES OF COMMERCIALLY PURE METALS (at 20°C)

Metal	Relative Electrical Conductivity (Copper = 100)	Relative Thermal Conductivity (Copper = 100)
Silver	106	108
Copper	100	100
Gold	72	76
Aluminum	62	56
Magnesium	39	41
Zinc	29	29
Nickel	25	15
Cadmium	23	24
Cobalt	18	17
Iron	17	17
Steel	13-17	13-17
Platinum	16	18
Tin	15	17
Lead	8	9
Antimony	4.5	5

copper is distinguished for its versatility, and it is this asset that is responsible for much of its widespread use.

Characteristics of the Commercial Types of Copper

The three basic types of commercial copper arise from the high affinity of molten copper for oxygen, and the methods employed for its control.

(1) *Electrolytic Tough-pitch Copper* (Type ETP)* can be cast with a level "set" by adjustment of the oxygen content between normal limits of 0.02 to 0.05 per cent. Because of its adaptability to high-tonnage melting and casting techniques it is the least expensive type to produce and has long been the standard variety for the production of wire, rod, plate, sheet, and strip. The presence of oxygen affects the mechanical properties to some degree, but it also renders certain impurities insoluble by converting them to oxides. This scavenging effect is beneficial both to high conductivity and to low annealing temperature (see Chapter 19).

At elevated temperatures solid tough-pitch copper is deoxidized by reducing gases. In the case of CO, which is insoluble in copper, the process takes place by diffusion of oxygen to the surface where it reacts to form CO_2, resulting in a gradual transition to the oxygen-free condition without physical damage. The same phenomenon has been observed in hydrogen atmospheres, but only under conditions where the relatively slow rate of delivery of oxygen to the outside surface by diffusion exceeds the available hydrogen, *e.g.*, at very low hydrogen pressures[2]. Most reducing atmospheres contain sufficient hydrogen to permit hydrogen embrittlement to proceed readily. Because of their small size and high mobility, the hydrogen atoms diffuse rapidly into the solid copper, and react with the internally dispersed Cu_2O to form steam at such disruptive pressures that the original structure is shattered beyond repair. Accordingly, tough-pitch copper cannot be used where joining processes or service conditions include this possibility.

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* Designations according to ASTM classification of coppers B 224-48T (see Table 14-1, p. 342).

(2) *Oxygen-free Copper* (Type OF) is produced either by melting in the presence of carbon or carbonaceous gases, and casting in a reducing atmosphere, or by coalescence of specially prepared and treated cathodes under heat and pressure. In the former method, the impurities are alloyed by the melting operation, resulting in higher annealing temperatures than are encountered with the ETP variety. The net change of conductivity is negligible, however, since the tendency for loss due to increased solubility of impurities can be offset by gains due to elimination of Cu_2O, and regulation to allow partial oxidation of some of the impurities, notably iron.

OFHC copper is used where a high-conductivity copper must withstand hydrogen atmospheres, for metal-to-glass seals in the electronic industry, for impact extrusion, and where high residual ductility is required in hard-temper material. It can also be modified during production by additions of silver, phosphorus, etc., as desired.

Coalesced copper (PDCP) is not melted during the processing cycle and the impurities mechanically trapped in the original cathodes are physically dispersed in unalloyed form in the product. As a result, this type of copper normally has a conductivity advantage of several tenths of a per cent, and a low annealing temperature. It is presently extruded to sizes for mill finishing and thus is not available in many of the standard dimensions associated with refinery shapes produced by casting. Alloying additions are also precluded by the nature of the operations.

The extrusion operation provides an excellent surface, free from laps and slivers which may act as points of weakness in insulated coatings. Consequently, a large proportion of coalesced copper is used for the manufacture of conductors in the form of wire, flat wire, bar, and strip. These products are also characterized by high residual ductility, resistance to hydrogen embrittlement, and suitability for metal-to-glass seals.

(3) *Deoxidized Coppers* (Types DLP and DHP) are produced by deoxidizing with sufficient phosphorus to insure combination with all of

the available oxygen. The high-conductivity type DLP must contain very little residual phosphorus, and the total content rarely exceeds 0.011 per cent P. Greater amounts are intentionally added to produce type DHP which may contain 0.015 to 0.035 per cent P, resulting in a conductivity range of 80 to 90 per cent IACS. A significant increase in annealing temperature is also obtained which permits soldering of hard-drawn products with minimum softening. The residual phosphorus is most beneficial in preventing the absorption of oxygen by the copper during hot-working and annealing operations, thus avoiding embrittlement during those subsequent processes which require heating in a reducing atmosphere. It is especially important to provide a *residual* deoxidizer in material to be welded by gas, carbon-arc, or metal-arc methods, where both embrittlement and porosity would result from oxidation. Consequently, the quantity of phosphorized copper used for tube manufacture alone exceeds that of all other oxygen-free or deoxidized types combined.

Table 17-2. The Properties of Copper

1. Melting point: 1083 ± 0.1°C (1981.4 ± 0.2°F)
2. Boiling point[30]: 2595°C (4703°F)
3. Vapor pressure vs. temperature (see ref. 6)
4. Coefficient of thermal expansion at 20°C[31]: 0.0000165
   0 to 300°C, $L_t = L_o [1 + (16.23t + .00483t^2) \times 10^{-6}]$.
   For 0 to 1000°C and [−23 to −223°C], see ref. 6
5. Solidification shrinkage: 4.92 per cent for oxygen-free and deoxidized types
6. Solidus temperature: 1065°C (1949°F) for type ETP
7. Specific heat: at 20°C (68°F)[32]: 0.092 cal per gram
   Specific heat, solid, 0 to t: $0.092 + 0.0000250t$ cal per gram
   Specific heat, liquid: 0.112 cal per gram
8. Latent heat of fusion[43]: 48.9 cal per gram
9. Latent heat of vaporization[30]: 1,150 cal per gram
10. Thermal conductivity: at 20°C[6], 0.934 cal per sq cm per cm per deg. C per sec
    (adjusted to electrical conductivity of 101 per cent)
11. Heat of oxidation[34]: Cu_2O, 334 cal per gram of Cu
    CuO, 607 cal per gram of Cu
12. Electrical resistivity *vs.* temperature (including liquid) (see ref. 6).
13. Temperature coefficient of electrical resistivity: at 20°C[7], 0.0068 microhm-cm
    per deg. C or 0.00060 ohm per meter-gram per deg. C.
14. Electrochemical equivalent: 0.3294 mg per coulomb for Cu^{++}
    0.6588 mg per coulomb for Cu^{+}
15. Electrolytic solution potential *vs.* hydrogen:
    Cu^{++}, minus 0.344 volt
    Cu^{+}, minus 0.470 volt
16. Temperature coefficient of solution potential *vs.* hydrogen[35]: minus 0.01 mv per
    deg. C

17. Hall effect[36]: minus 5.24 × 10^{-4} volt; 3,000 to 8,116 gausses
18. Reflectivity *vs.* wave length (see ref. 6)
19. Refractive index (see ref. 6)
20. Absorptive index (see ref. 6)
21. Emissivity[37]:

at wave length Å:	*7,000*	*6,500*	*6,000*	*5,500*	*5,000*
% emissivity at 1000°C (1832°F)	8.7	11.2	18.5	31.3	40.4
% emissivity at 1125°C (2057°F)	11.8	14.8	20.5	29.3	38.7

22. Magnetic susceptibility[38, 39, 40]:

Temperature:	−259 to −253°C	18°C	1080°C	1090°C
cgs units × 10^{-6}:	−0.097	−0.080	−0.077	−0.054

23. Velocity of sound[41]: 12,700 ft. per sec. at 20°C
24. Crystal structure[31]: face-centered cubic, a = 3.6080 kX
    Slip plane (primary): (111)
    Twinning plane: (111)
    Minimum interatomic distance[31]: 2.551 kX
25. Poisson's ratio[42]: 0.33 ± 0.01
26. Viscosity[6]: at *1145°C (2093°F), 0.0341 cgs units*
27. Surface tension[6]: at 1150°C (2102°F), 1104 dynes per cm

Conductivity—Electrical and Thermal

The electrical conductivity of standard copper was defined in 1913 by the International Electrotechnical Commission. The resulting International Annealed Copper Standard (IACS) is 0.15328 ohm (meter-gram) at 20°C; that is, a copper wire 1 meter long, weighing 1 gram, and having a resistance of 0.15328 ohm at 20°C. A standard density of 8.89 grams per cubic centimeter was also adopted to permit expression of the standard in terms of both mass and volume units as in the following equivalents:

0.15328 ohm (meter-gram), 875.20 ohms (mile, pound),
0.017241 ohm (meter, sq mm), 1.7241 microhm-cm,
0.67879 microhm-inch, and 10.371 ohms (mil, foot),
all at 20°C[3].

To obtain the conductivity of any given sample, the standard resistivity is divided by the resistivity of the unknown, and the results expressed as a percentage. Present-day ASTM specifications require all copper intended for electrical use to meet a 100 per cent conductivity minimum, and the values found for the various types of commercial high-conductivity copper generally fall between 100.5 and 101.8 per cent. Very high-purity copper prepared for research use has a conductivity of 102.3 per cent of the standard[4].

Fortunately, copper may be extensively cold worked with but a slight loss of conductivity as compared to that experienced with the brasses and other alloys. Figure 17-1 is a composite of the results obtained by

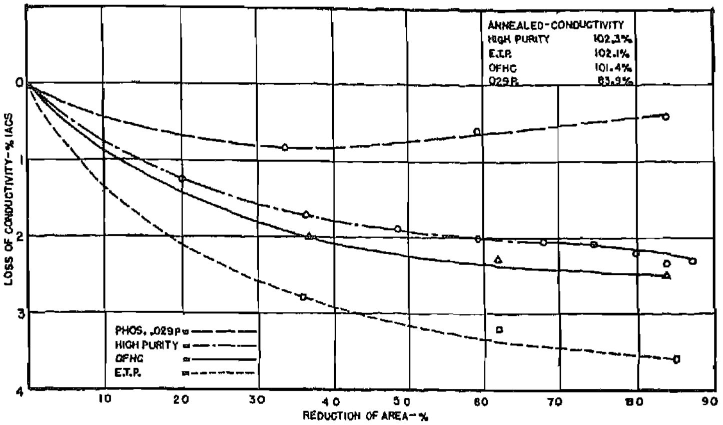

Figure 17-1. Decrease in conductivity of copper through cold reduction.

Crampton, Burghoff, and Stacy[5] and the data for high-purity copper[4]. Some variation between commercial lots is to be expected; for instance, in the experience of the writer the average conductivity difference between annealed and hard-drawn tough-pitch copper is 2.7 per cent, within a general range, which is controlled by impurity differences, of 2.5 to 3.5 per cent IACS. The presence of added elements often alters the magnitude of the loss very significantly, as illustrated by the curve for phosphorized copper in Figure 17-1. An unusual effect is obtained from additions of arsenic, which up to 0.08 per cent cause the difference to diminish to zero, and in greater amounts result in higher conductivities in the hard-drawn material[26].

The effects of even the most drastic cold working are considerably less than those due to changes of temperature; upon heating from 20°C to the melting point at 1083°C, the electrical conductivity drops from 100

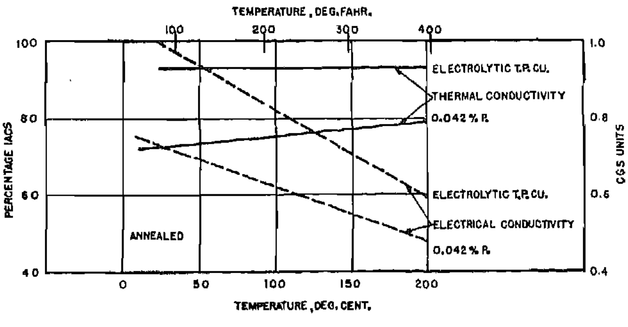

Figure 17-2. Variation of electrical and thermal conductivities of copper with temperature.

to about 15 per cent[6]. However, the effect on thermal conductivity is much smaller, as will be seen from Figure 17-2, which compares data covering the performance range normally encountered in product applications.

Mechanical Properties

High-purity copper is so ductile that it is difficult to determine the existence of a finite limit beyond which it cannot be cold worked. No evidence of such a limit has been observed in wires drawn 99.4 per cent, which had developed a tensile strength of 75,000 psi[4]. In commercial tube practice, both phosphorus-deoxidized and OFHC coppers may be cold drawn as much as 95 per cent, and in wire drawing, tough-pitch copper is frequently carried beyond 90 per cent reduction, although in all of these operations other considerations often dictate the use of a more moderate working schedule.

The tensile strength and elongation values obtained by cold working the three basic commercial types are identical from a practical standpoint. Figure 17-3 compares the results obtained by Wilkins and Bunn[7]

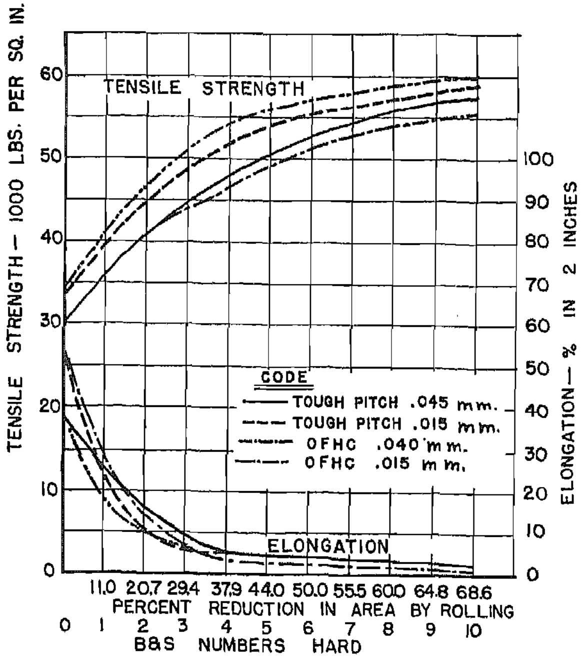

FIGURE 17-3. Effect of cold work on the tensile strength and elongation of tough-pitch and oxygen-free copper.

on rolled strip manufactured from types ETP and OF. Webster, Christie, and Pratt[8] have published data on these, and type DHP as well, obtaining similar minor differences from samples in the form of rods. This equivalence in mechanical properties is largely responsible for continuance of the historical tendency to consider both oxygen- and phosphorus-bearing coppers as commercial forms of the metal, and to reserve alloy designation for products having more pronounced alteration of physical characteristics. Variations in grain size, for instance, may result in more significant differences in these properties (Figure 17-3), particularly in the annealed tempers, which are defined by grain size, and where its control is required to insure satisfactory performance in such operations as the winding of wire coils, the bending of tubing, and the drawing of sheet-metal objects.

Nevertheless, those engaged in processing these forms of copper recognize the existence of basic advantages and disadvantages peculiar to type. Each variety can be fabricated to shapes that require remarkable ductility, but the presence of oxygen in tough-pitch copper, for instance, may so affect the capacity of the material for further cold working that severe forming operations, which are permissible with the oxygen-free or deoxidized types, cannot be carried out successfully in the harder tempers. The measurement of residual ductility is not a simple task; Webster, Christie, and Pratt have pointed out that higher reduction-of-area values are obtained from types OF and DHP than from ETP in tensile tests after various degrees of cold reduction, and that the progressively increasing differential in these values is much more relevant to the observed differences in practice than are elongation measurements.

Bend tests and twist tests are similarly illustrative[9], but the procedures are not standardized, and the data are usually regarded as even more qualitative in nature. Fortunately, our quantitative shortcomings in the field of direct measurement are capably replaced by a considerable amount of extremely useful empirical information based on experience in such operations as flaring, flanging, spinning, drawing, and bending, by means of which many specific fabricating problems are solved.

In the interest of brevity no attempt will be made to reproduce here the comprehensive and detailed presentation of the mechanical properties published by Wilkins and Bunn[7]. The reader is referred to this source for specific data covering such properties as hardness, elastic limit, yield strength, stress-strain relations, and general annealing behavior as influenced by degree and method of cold work, grain size, and type of copper. For general use, a classification of mill tempers is listed in Table 17-3 and representative properties for tough-pitch copper in Table 17-4[10].

TABLE 17-3. MILL TEMPERS

Standard Temper Designation	Reduction in B & S Gage Numbers	Plate, Sheet, and Strip % Reduction in Thickness	Wire % Reduction in Area
⅛ hard	½	6	11
¼ hard	1	11	21
½ hard	2	21	37
¾ hard	3	29	50
Hard	4	37	60
Extra hard	6	50	75
Spring	8	60	84
Extra spring	10	68	90
Rivet temper	—	—	7
Screw temper	—	—	15

In the manufacture of sheet and strip the temper designations are based on equivalent percentage reduction, and therefore the tensile properties of materials having the same temper, but different gage, are reasonably similar. There are limits and exceptions, however, particularly as thickness (or diameter of rod) increases, which make it advisable to consult the appropriate specifications for guidance. In the American wire industry, the tensile properties of soft, medium hard, and hard-drawn copper wire are defined by ASTM specifications B1, B2, and B3, in which the tensile strength and elongation values are specified for each size of the American wire gage. In hard-drawn wire, maximum strength is desired, and consequently, the smaller sizes, which receive more total reduction, are required to have higher tensile strengths than the larger sizes.

Effect of Temperature

Figures 17-4[11, 12] and 17-5[13] plot the tensile properties of annealed copper at temperatures from −180 to 700°C (−290 to 1290°F), the beginning of the hot-working zone. The complete absence of any brittle range is well illustrated by these data, a fact which is of prime importance to the casting and working behavior. Similar information for cast copper is also available[13] and while the tensile strength of castings generally approximates 22,000 psi, a considerable variation can be experienced depending on the technique employed to produce them. The heating of work-hardened coppers for the purpose of annealing involves the complications of the process of recrystallization, which is so materially influenced by the effects of impurities that it will be considered in Chapter 19.

TABLE 17-4. MECHANICAL PROPERTIES OF COPPER

Form	Size of Section	Temper	Tensile Strength	Yield Strength (½% Extension under Load)	Contraction of Area	Elongation in 2 in	Rockwell Hardness			Shear Strength	Endurance Strength	
			psi	psi	%	%	F	B	30T	psi	psi	Million Cycles
Flat products	0.040 in.	0.050 mm	32,000	10,000		45	40			22,000		
		0.025 mm	34,000	11,000		45	45			23,000	11,000	100
		Eighth hard	36,000	28,000		30	60	10	25	25,000		
		Quarter hard	38,000	30,000		25	70	25	36	25,000		
		Half hard	42,000	36,000		14	84	40	50	26,000	13,000	100
		Hard	50,000	45,000		6	90	50	57	28,000	13,000	100
		Spring	55,000	50,000		4	94	60	63	29,000	14,000	100
		Extra spring	57,000	53,000		4	95	62	64	29,000		
		As hot rolled	34,000	10,000		45	45			23,000		
	0.250 in.	0.050 mm	32,000	10,000		50	40			22,000		
		Eighth hard	36,000	28,000		40	60	10		25,000		
		Quarter hard	38,000	30,000		35	70	25		25,000		
		Hard	50,000	45,000		12	90	50		28,000		
		As hot rolled	32,000	10,000		50	40			22,000		
	1.0 in.	Hard	45,000	40,000		20	85	45		26,000		

TABLE 17-4. MECHANICAL PROPERTIES OF COPPER (Cont'd)

Form	Size of Section	Temper	Tensile Strength	Yield Strength (½% Extension under Load)	Contraction of Area	Elongation in 2 in.	Rockwell Hardness			Shear Strength	Endurance Strength	
			psi	psi	%	%	F	B	30T	psi	psi	Million Cycles
Rod	1.0 in.	0.050 mm	32,000	10,000	70	55	40			22,000		
	0.250 in.	Hard (40%)	55,000	50,000		10	94	60		29,000		
	1.0 in.	Hard (35%)	48,000	44,000	55	16	87	47		27,000	17,000	300
	2.0 in.	Hard (16%)	45,000	40,000		20	85	45		26,000		
	1.0 in.	As hot rolled	32,000	10,000	70	55	40			22,000		
Wire	0.080 in.	0.050 mm	35,000			35*				24,000		
		Hard	55,000			1.5**				29,000		
		Spring	66,000			1.5**				33,000		
Tube	1.0 in. O.D. x 0.065 in.	0.050 mm	32,000	10,000		45	40			22,000		
		0.025 mm	34,000	11,000		45	45			23,000		
		Light drawn (15%)	40,000	32,000		25	77	35	45	26,000		
		Hard drawn (40%)	55,000	50,000		8	95	60	63	29,000		
Shapes	0.500 in.	0.050 mm	32,000	10,000		50	40			22,000		
		Hard (15%)	40,000	32,000		30		35		26,000		
		As hot rolled	32,000	10,000		50	40			22,000		
		As extruded	32,000	10,000		50	40			22,000		

*Elongation in 10 inches. **Elongation in 60 inches.

The values listed above represent reasonable approximations suitable for general engineering use. Due to commercial variations in composition and to manufacturing limitations, *they should not be used for specification purposes. See applicable A.S.T.M. specification reference.*

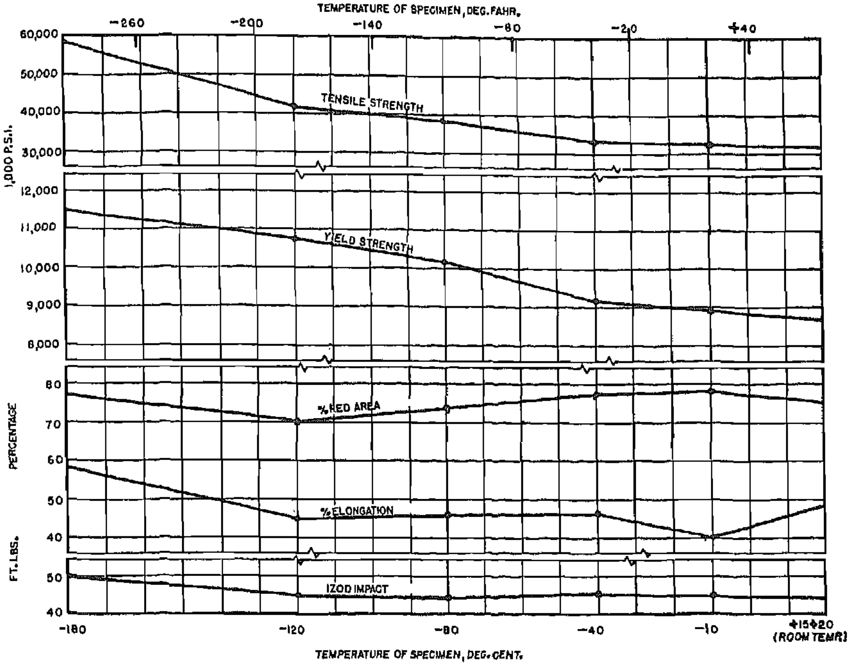

FIGURE 17-4. Tensile properties of annealed copper at low temperatures.

Creep Strength

Under loads of long duration copper, as is true of other metals, plastically deforms, or creeps, at rates which are dependent upon such variables as temper, chemical composition with respect to alloying elements or impurities, previous thermal history, grain size, temperature, etc. A recently completed study by Blank and Burghoff[14] summarizes the creep characteristics of several types of copper according to Table 17-5. The effects of phosphorus and arsenic additions will be noted. Silver and cadmium are also known to increase the creep strength of coppers to a marked degree[15, 16, 17, 18] and have the additional advantage of negligible loss of conductivity. Such coppers, for instance, can be used to resist the tendency for the windings of large rotors to lose their original shape under the centrifugal loads encountered in service.

Impact Strength

Due to its inherent toughness and freedom from brittle tendencies at low temperatures, copper has good impact properties. Figure 17-6 compares some results obtained from three types of copper in fabricated rod form[9]. Since only two tempers were tested the curves are represented by broken lines and are intended only to indicate the general effect of work hardening. The comparison of impact data for copper is complicated by the fact that fracture is normally not obtained from Izod or Charpy specimens. The published data are not plentiful, but additional information is available on sheet[19], on rods and castings at elevated temperatures[13], and on tension impact[20].

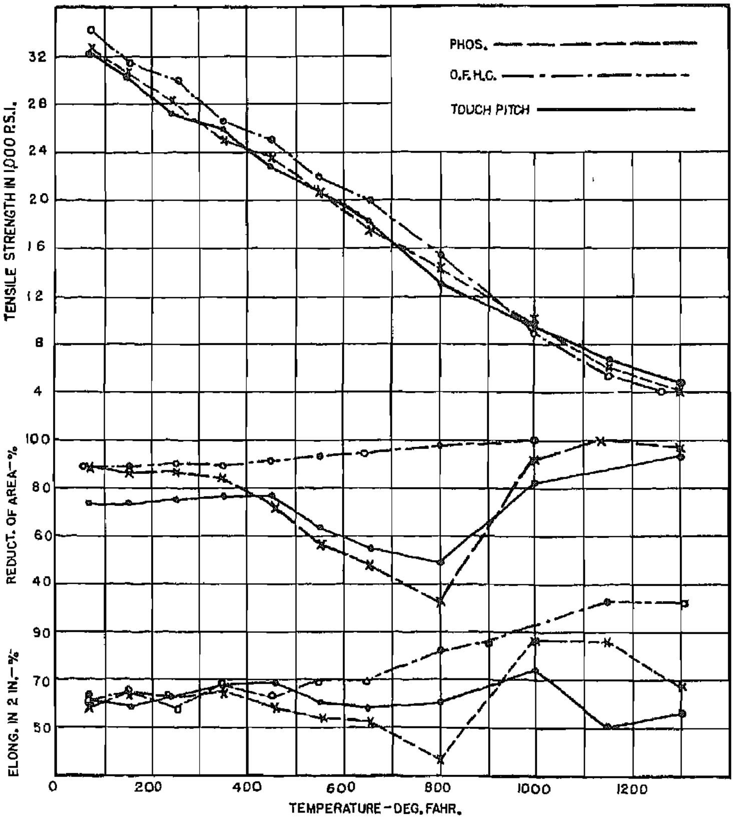

FIGURE 17-5. Effect of rise in temperature on the tensile properties of copper.

Stress-Strain Relations

The modulus of elasticity of copper apparently increases as a result of work hardening, although the reverse is true of its alloys. Smith and Van Wagner[21], working with commercially produced rods, determined the modulus of elasticity, elastic limit, and proportional limit for both tough-pitch and oxygen-free copper. Table 17-6 presents these data, and

TABLE 17-5. COMPARISON OF SEVERAL TYPES OF COPPER WITH RESPECT TO TENSILE PROPERTIES AND ELECTRICAL CONDUCTIVITY AT 21°C (70°F) AND CREEP STRENGTH AT 150, 200, AND 260°C (300, 400, AND 500°F)

ASTM Designation	TEMPER		Tensile Strength at 70°F, psi	Yield Strength at 0.5 per cent Extension under Load at 70°F, psi	Creep Strength, Stress, psi, for Creep Rate of 0.01 per cent per 1000 hr			Electrical Conductivity at 70°F, per cent IACS
	Annealed	Drawn						
	Avg. Grain Size, mm	Reduction, per cent			300°F	400°F	500°F	
ETP	0.025		35,100	7,200	2,950	1,300	350	100.9
OF	0.025		34,500	7,900	3,600	1,500	400	101.3
DLP	0.013		36,500	12,000	7,200	2,100	700	100.1
DHP	0.015		34,800	8,600	5,100	2,550	650	89.0
	0.032		33,300	5,850	5,400	2,650	900	89.0
	0.070		32,200	4,550	7,200	4,000	2,000	88.6
DPA	0.045		35,000	6,100	8,400	5,200	2,600	45.3
ETP		84	55,400	50,000	9,400	2,100		99.1
OF		84	54,500	49,500	8,300	1,750		99.5
DLP		84	57,500	54,000	21,000	5,200	600	98.3
DHP		84	56,400	52,000	33,500	2,500[a]	1,000[a]	88.5
DPA		84	60,900	55,500	40,000	27,500	2,000[b]	46.0

[a] By extrapolation of log stress-log creep-rate curve.

[b] Produces third stage of creep, accelerating creep rate.

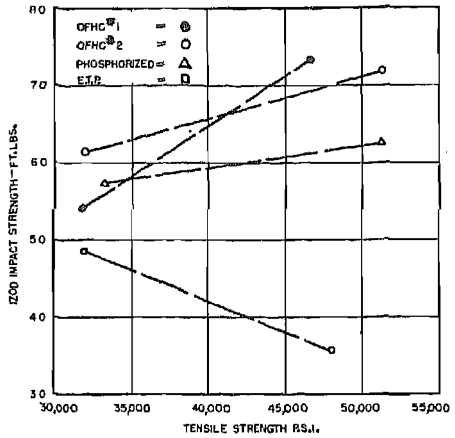

FIGURE 6

FIGURE 17-6. Relationship between tensile and impact strength for different types of copper in the form of rod.

Table 17-7 includes the values of stress, strain, set, and offset corresponding to various yield-strength criteria. Phillips and Smith[22], employing commercial hard-drawn and annealed tough-pitch wires, obtained respective instantaneous modulus values of 18,000,000, and 13,400,000 psi using a highly accurate technique based on a 60-inch gage length.

TABLE 17-6. SOME COMPARATIVE STRESS-STRAIN RELATIONS OF TOUGH-PITCH AND OXYGEN-FREE COPPER

	Tough-pitch Copper		Oxygen-free Copper	
	Hard	Annealed	Hard	Annealed
Modulus of elasticity, million psi	16.95	15.82	17.54	16.20
0.0002% *offset—stress, psi*				
Initial	8,300	1,150	8,300	1,400
Strained*	13,400	3,300	15,000	3,300
0.002% *offset—stress, psi*				
Initial	12,850	1,900	15,400	1,950
Strained*	21,500	4,720	24,800	4,500
0.0002% *permanent set—stress, psi*				
Initial	5,000		5,500	
Strained**	21,000		21,000	
0.002% *permanent set—stress, psi*				
Initial	13,500		14,200	
Strained**	34,800		38,200	
Yield strength (0.5% strain), psi	46,000	5,500	47,000	5,000
Tensile strength, psi	46,900	31,500	47,500	30,900
Elongation in 2 in., %	14.8	53.0	20.5	60.0
Reduction of area, %	58.5	71.4	86.4	92.1

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* Stress for stated offset after prestraining to 0.5 per cent extension. See Table 17-7 for resulting permanent set.

** Stress for stated permanent set after prestressing to produce a permanent set of 0.10 per cent.

TABLE 17-7. SOME COMPARATIVE YIELD-STRENGTH DATA FOR TOUGH-PITCH AND OXYGEN-FREE COPPER

	Electrolytic Copper	OFHC Copper
0.5% total strain		
Stress at 0.5% strain	46,000 psi	47,000 psi
Offset at 0.5% strain	0.229%	0.232%
Resulting permanent set	0.212%	0.222%
0.1% set		
Stress for 0.1% permanent set	44,300 psi	45,000 psi
0.1% offset		
Stress	43,700 psi	44,600 psi
Total strain	0.359%	0.355%
0.2% offset		
Stress	45,700 psi	46,800 psi
Total strain	0.473%	0.468%

Density

The density of copper varies with its composition and method of preparation, and with pure copper values have been obtained as high as 8.9592 grams per cubic centimeter at 20°C[4]. Commercial refinery shapes of deoxidized and oxygen-free copper having densities in the range 8.90 to 8.92 are produced by several processes. Tough-pitch castings normally run nearer 8.50 + grams per cubic centimeter[23], reflecting the necessity for a shape with a level set to contain porosity equal to the solidification shrinkage of the metal.

Hot working largely eliminates the density differences which exist in the cast shapes and results in average densities of 8.93 for annealed tough-pitch copper and 8.94 for copper[9] which is oxygen-free. Upon cold working, the density decreases by an amount which appears to be additionally influenced by oxygen and impurity contents[4], *viz.*, a decrease of .0033 grams per cubic centimeter (0.037 per cent) for pure copper, and .03 grams per cubic centimeter (0.34 per cent) for the electrolytic tough-pitch variety[19, 24, 25], after 90 per cent cold reduction.

At higher temperatures the density decreases in accordance with Figure 17-7[26, 27]. At higher pressures, the density increases in relation to the volume compressibility, which may be computed from the formula[28]

$$AV/Vo = 10^{-7}P(7.32 - 2.7 \times 10^{-6}P)$$

where P is the pressure in kg per sq cm.

Table 17-2 gives data on those additional properties of copper which can be readily tabulated. Much of the information has been determined for tough-pitch copper only, and the data can be assumed to refer to this type unless there are notations to the contrary. Where graphs are neces-

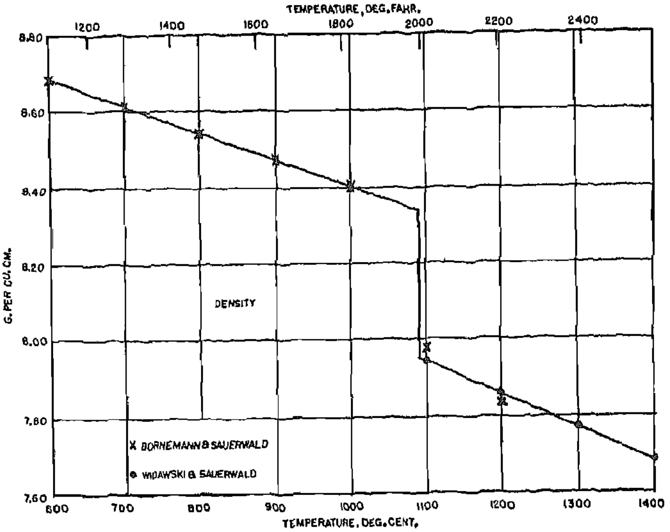

FIGURE 17-7. Change in density of copper with temperature.

sary to present property ranges, the reader is referred to "The Metals Handbook" for the available coverage.

Special Types of Copper

Silver-bearing Copper (Types STP, OFS, DPS) produced by fire refining (Lake copper) and by additions of silver to electrolytic copper is widely employed for uses requiring a combination of high conductivity and high annealing temperatures. If the annealing temperature of ETP copper in the hard temper is taken as 200 to 225°C (390 to 440°F), the addition of 10 to 12 oz Ag per ton will result in an increase to 325 to 350°C (620 to 660°F) with negligible sacrifice of conductivity. (See also Chapter 19 and Gregg[29], p. 121). Larger additions have proportionately less effect on softening temperature, but are used for unusual requirements, and for their beneficial effect on long-time stress-rupture properties, as mentioned previously.

Arsenical Copper (Types ATP, DPA, SATP) containing from 0.25 to 0.50 per cent As has long been used for structural purposes, although it is more popular in British than American practice. Where produced as a fire-refined product it represents a useful economic short-cut since arsenic removal requires costly fluxing. Flat products and tubing are made from the tough-pitch, deoxidized, and silver-bearing varieties, which have slightly higher tensile and fatigue strengths than the purer electrolytically refined metal. These advantages become more significant in elevated temperature uses, where the increase in annealing temperature produced by arsenic, and the additional benefits conferred by the use of phosphorus and silver, result in advantageous properties. The fabricating properties and corrosion resistance of these variations are excellent, but the conductivity of copper containing 0.50 per cent As is reduced to about 40 per cent of the standard[29].

Tellurium Copper (Types TETP, OFTE, DPTE) has become the most widely adopted of the three free-machining types based on the addition of such insoluble elements as tellurium, selenium, and lead, which act as chip breakers. The addition of 0.5 per cent Te permits the manufacture of mill shapes having a conductivity of 98 per cent and a machinability rating of 90 (free-cutting brass = 100; copper = 20). However, the normal product is deoxidized with phosphorus and the conductivity is closer to 85 per cent.

The overlapping terminology of the nonferrous industry results in some widely used designations such as beryllium copper and cadmium copper for materials which cannot be classified other than as alloys. Cadmium copper is a term used for a high-strength trolley-wire alloy. Thus, the recent appearance of a type of copper containing very small quantities of cadmium (useful for transmission lines requiring a high softening temperature and high conductivity at low cost) emphasizes the utility of the specific type of designation now being evolved by the American Society for Testing Materials.

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Chapter 18

Chemical Properties and Corrosion Resistance of Copper and Copper Alloys

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General Consideration of the Chemical Properties of Copper

Copper is the first member of subgroup IB of the periodic table, being followed by silver and gold. It was formerly customary to place these elements in group I of the table with the subgroup IA elements lithium, sodium, potassium, rubidium, and caesium. There are virtually no similarities between copper, silver, and gold on the one hand and the alkali metals on the other, however, and recent versions of the periodic table, based on electronic structures, place the elements in a more logical sequence; there is now no need to stretch the imagination in attempting to find similarities between these two groups of elements. Compared with the extremely reactive alkali metals, the coinage metals copper, silver, and gold are very stable.

Each of the three forms a univalent series of salts, but copper also forms a bivalent series and gold a trivalent series, both of which are more stable than the corresponding univalent compounds. This variable valency is, of course, characteristic of most elements which do not have an octet of electrons in their outermost shell but one. The atomic number of copper is 29 and the electronic configuration is 2:8:18:1. Loss of the outermost electron produces the cuprous ion Cu^+, and a second electron may be lost in the formation of the cupric ion Cu^{++}. The formation of these two ions is an important factor in considering the corrosion behavior of copper. As with other metals exhibiting variable valency, additional electrode reactions are possible above those which can occur with metals which exhibit only a single valency.

Some of the characteristic features of the chemistry of the coinage metals may be summarized as follows:

(1) They occur in the uncombined state in nature and are relatively easily obtained by reduction of the compounds.

(2) They are not very active chemically. As the atomic weight increases the chemical activity decreases.

(3) They oxidize very slowly in air at ordinary temperatures.

(4) *Their oxides and hydroxides are but feebly basic.*

(5) Insoluble chlorides are formed, *e.g.*, CuCl.

(6) Complex ions are readily formed, *e.g.*, $[Cu(CN)_2]^-$.

(7) Complex cations are formed with ammonia, *e.g.*, $[Cu(NH_3)_4]^{++}$.

In the electrochemical series of elements copper is near the noble end and will not normally displace hydrogen from acid solutions. Indeed, if hydrogen is bubbled through a solution of a copper salt, copper is slowly deposited (more rapidly if the process is carried out under pressure).

General Consideration of the Corrosion Behavior of Copper and Copper Alloys

One of the main reasons for the successful use of copper and copper-base alloys on so wide a scale is the excellent resistance to corrosion displayed by these materials in a wide range of environments. As copper is not an inherently reactive element, it is not surprising that the rate of corrosion, even if unhindered by films of insoluble corrosion products, is often not high. Nevertheless, although the breakdown of a protective oxide film on copper is not likely to lead to such rapid attack as with a more reactive metal such as, say, aluminum, in practice the good behavior of copper (and more particularly of some of its alloys) depends to a considerable extent on the maintenance of an inhibitive film of oxide or other insoluble corrosion product.

Many of the alloys of copper are more resistant to corrosion than copper itself, due to the incorporation of either relatively corrosion-resistant metals such as nickel or tin, or metals such as aluminum or beryllium which would be expected to assist in the formation of protective oxide films. Several of the copper alloys are liable to undergo a selective type of corrosion in certain circumstances, the most notable example being the dezincification of brasses. Some alloys again are liable to suffer stress corrosion by the combined effects of internal or applied stresses and the corrosive effects of certain specific environments. The most widely known example of this is the season cracking of brasses. In general brasses are the least corrosion-resistant of the commonly used copper-base alloys.

The various grades of copper available (tough-pitch or deoxidized, with or without arsenic, etc.) do not differ in practice to any marked extent in their corrosion resistance, and a choice is usually based on other grounds. The references which follow to the corrosion behavior of copper may therefore be taken to apply broadly to all types of copper.

The choice of alloys for any particular application is often based on the desired physical, mechanical, or metallurgical properties. Within these limits, however, a range of materials is usually available. It is essential that at the very earliest stage the choice of materials and the details of design of the installation should be considered from the point of view of corrosion, if the best performance is to be obtained in service. This is particularly true of copper alloys, where protective measures are not normally applied.

In ensuing pages of this chapter the behavior of copper and its alloys in several important environments will be briefly considered. Emphasis will be placed on underlying principles and no attempt will be made to give a complete collection of quantitative data, but sufficient references to the literature will be given to enable most of the important data to be found. A number of general summaries of the corrosion behavior of copper are available[1, 2, 3, 4, 5, 6, 6a].

Copper and Copper Alloys Versus Various Chemicals

Detailed information on the action of a wide range of chemicals on copper and copper alloys is given in a number of publications, particularly those listed under references 1 to 13.

When contemplating the use of copper-base materials for industrial purposes it is necessary to bear in mind that even though a satisfactory life of the component may be obtained, trouble can arise from other causes:

(1) Copper compounds can only be tolerated in small amounts in potable waters or substances to be consumed[1].

(2) Copper compounds are highly colored and a very small amount of corrosion may lead to staining and discoloration of products.

(3) Stimulation of the corrosion of vital parts made of more anodic metals may occur if they are connected to copper.

(4) Very small amounts of copper taken into solution may cause considerable corrosion of more anodic metals elsewhere in the system, particularly zinc[14], aluminum[131], and sometimes steel[15]. Small particles of copper deposited from solution set up local cells which cause rapid pitting.

Despite these qualifications copper and its alloys are used extensively and successfully in much chemical equipment. Uses include condensers and evaporators, pipelines, pumps, fans, vacuum pans, fractionating columns, etc. Tin bronzes, aluminum bronzes, and silicon bronzes are used in some circumstances because of better corrosion resistance than copper or brasses.

Acid Solutions. Since copper does not normally displace hydrogen even from acid solutions it is usually virtually unattacked in most nonoxidizing solutions. Most solutions which have to be handled contain dissolved air, however, and this will cause depolarization of the local cathodes and enable some corrosion to take place. It is difficult, therefore, to lay down any general recommendations for the use of copper in acid solutions, since the rate of attack depends so greatly on the particular circumstances. Under fairly mild conditions copper or copper alloys are successfully used for handling solutions of hydrofluoric[7, 16], hydrochloric[2, 3, 4, 7, 17], sulfuric[2, 3, 4], phosphoric[2, 3, 7, 18], and acetic and other fatty acids [2, 3, 4, 7, 19]. The severity of the conditions increases, in general, if the concentration of acid increases, the temperature rises, and the amount of aeration[20, 21] and the speed of flow increase. Tin bronzes[2], aluminum bronzes[1], silicon bronzes[1, 2], and cupronickels[2] are among the copper alloys most resistant to acids. Brasses should not normally be used. All copper-base materials are attacked rapidly by oxidizing acids such as nitric, strong sulfuric, etc.

Neutral and Alkaline Solutions. Copper-base materials are also attacked to some extent by aerated alkaline solutions[2, 3, 22], but may be used in some cases depending on the precise conditions. Copper and copper alloys should normally be avoided if ammonia[2, 3] is present, owing to the danger both of general corrosion and, if components are under stress, of stress corrosion.

Copper can be expected to be satisfactory for handling solutions of most neutral salts[1, 2, 3, 7, 23] unless aeration and turbulence are excessive. Exceptions are those salts which form complexes with copper, such as cyanides, and solutions containing oxidizing agents, such as ferric or stannic compounds[2].

Other Chemicals. Copper and copper alloys are unsuitable for handling hydrogen peroxide[7, 24] or molten sulfur[7, 25]. Hydrogen sulfide accelerates corrosion of most copper-base materials. In its presence brasses high in zinc are usually found to behave better than other copper alloys[2].

Halogens have little action on copper at room temperature when dry, but are corrosive when wet. Hypochlorite solutions are corrosive[26]. The action of organic compounds is varied[2, 7]. Corrosion sometimes occurs with halogenated compounds or when acids are present. Copper and copper alloys are extensively and successfully used in refrigeration systems employing various organic refrigerants (*e.g.*, CCl_2F_2), however. Corrosion of copper alloys by hydrocarbon oils containing sulfur and sulfur compounds can be serious[1]. The effects of synthetic detergents on copper have been investigated by Holness and Ross[27]. A number of authors[3, 7, 28, 29, 30] have discussed various aspects of the behavior of copper and its alloys in the food-processing industry.

Copper and Copper Alloys in Sea Water

Vast quantities of copper and copper alloys are used in ship's machinery and fittings and in power stations. One of the most important applications is for tubular-type heat exchangers such as condensers, drain coolers, oil and water coolers. When sea water is the cooling medium serious risk of corrosion from the cooling water side arises unless correct materials and design are employed. Many scores of miles of copper-alloy condenser tubes condensing steam from the turbines are often installed in the main condensers of a single vessel or power station. Many other sea-water carrying pipes and components are also frequently made of copper or copper alloys. Corrosion problems in the past have been very serious and while many have been successfully solved, a number still remain. Surveys of the present position in this field have been given recently by several authors[31, 32, 33, 34, 132]. Heat-exchanger tubes with sea-water cooling are also used in large quantities in oil refineries[35, 36, 37].

The main types of corrosion which copper or copper alloys may suffer in sea water may be briefly summarized as follows:

(1) *Dezincification of Brasses.* When this occurs regions of the brass become replaced by a porous mass of copper which, though retaining the shape of the original article, has virtually no strength. There has long been discussion as to whether the process occurs by selective corrosion of the zinc in the brass leaving the copper behind, or whether complete dissolution of the brass occurs, followed by redeposition of copper. Some workers now hold that both processes may occur in different circumstances. The mechanism of the process has been discussed by Evans[1], Fink[38], Polushkin and Shuldener[56], and others.

Dezincification may proceed fairly uniformly over the surface, and this "layer type" is usually less dangerous than the localized "plug type" which more often occurs[39]. The zinc corrosion products which accompany dezincification are swept away, or in relatively stagnant conditions form voluminous deposits on the surface which may lead to blockages. With a single-phase brass the whole of the metal in the corroded areas is affected, but with a two-phase brass the zinc-rich β phase is preferentially attacked as shown in Figure 18-1. Eventually the α phase may be attacked as well. In general the risk of dezincification increases as the zinc content rises, and great care needs to be exercised in making brazed joints with a high-zinc (*e.g.*, 50 per cent) brazing metal, if they are to be exposed to sea water. A properly designed capillary joint should last for some time, but it is often preferable to use a different type of jointing metal (*e.g.*, silver solder).

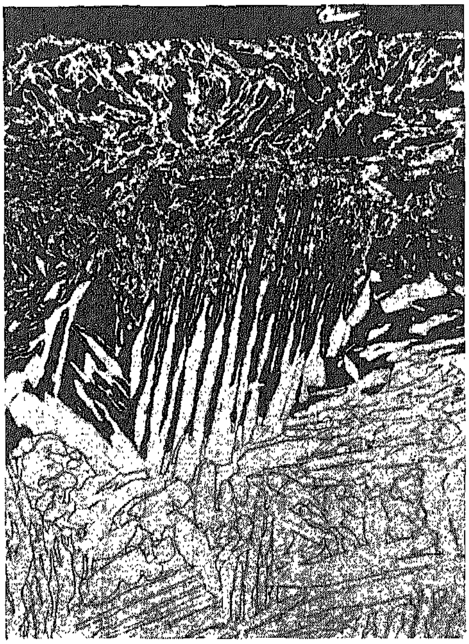

FIGURE 18-1. Dezincification of two-phase brass, showing preferential attack of the beta phase. Magnification 75X.

Factors connected with the environment which favor dezincification are high temperature, high chloride content of water, low water speed, and particularly the occurrence of deposits on the metal surface or crevices (*i.e.*, a low degree of aeration).

A small addition of arsenic (0.02 to 0.06 per cent in alpha brasses) will inhibit dezincification[40, 41] and it is claimed that additions of similar amounts of antimony or phosphorus have a similar effect. Very occasionally, inhibited alpha brasses corrode with the formation of redeposited copper, but in such cases there is usually some doubt whether a true dezincification reaction is involved. In general, for all practical purposes it may be considered that inhibited alpha brasses are immune to dezincification. This is particularly true of arsenical brasses, with which there has been the most experience[42].

The problem of dezincification of two-phase brasses is more difficult. Although various additions, including arsenic, have been advocated from time to time, most workers appear to agree that nothing is at present known which will render alpha-beta brasses immune to dezincification under all conditions of exposure. The addition of 1 per cent tin markedly reduces the rate of dezincification and naval brass (61-38-1) is attacked considerably more slowly than 60-40 brass under the same conditions. Some of the complex high-strength two-phase brasses containing tin, aluminum, iron, manganese, etc., appear to have relatively good resistance to dezincification.

It has been stated that types of attack analogous to dezincification can occur with aluminum bronzes, tin bronzes, and cupronickels, but these occurrences are comparatively rare.

(2) *Impingement Attack.* When moving water flows over copper or copper alloys the turbulence may be sufficient to cause breakdown of the surface film. This is particularly likely to happen if air bubbles which are entrained in the water break as they hit the metal surface. The resulting corrosion is characteristic, producing clean-swept pits, often of a "horseshoe" shape as shown in Figure 18-2. This type of attack was first described by Bengough and May[40, 43]. The action can be very rapid, the local anodes being depolarized by the continuous removal of metal ions and corrosion product, and the local cathodes by the dissolved oxygen in the rapidly moving well-aerated water stream.

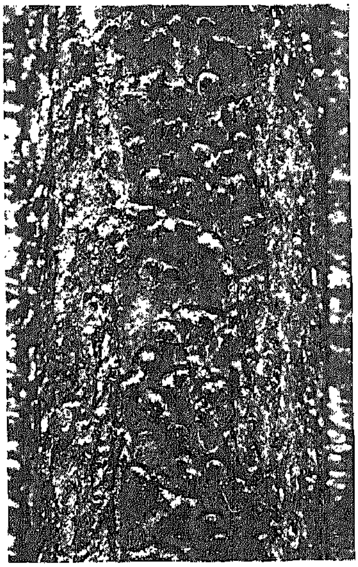

FIGURE 18-2. Typical impingement attack on admiralty-brass condenser tube from naval vessel. Magnification 2.5X.

Factors which tend to increase the severity of impingement attack are increase of water speed and particularly of local turbulence, pollution of the sea water, and, within certain limits, increase of the amount of entangled air bubbles and of the size of the bubbles, and decrease of temperature.

A laboratory test designed to imitate the conditions occurring in condenser tubes in practice was first described by May[43] and the newer versions of this "jet impingement apparatus" have recently been described[44]. Some of the testing equipment in use in the United States has also been described[45]. Use of the jet impingement apparatus has been an important factor in the development of alloys resistant to impingement attack.

(3) *Deposit Attack and Pitting.* When water speeds are low and deposits settle on the surface, pitting of copper and copper alloys is liable to occur owing to differential aeration effects. In sea-water systems trouble is particularly likely to occur under dead barnacles or shell fish, the decomposing organic matter assisting corrosion. Pitting is much more likely to occur in polluted in-shore waters, particularly those containing hydrogen sulfide, than in clean sea water from the open sea. In such contaminated waters deposits are not essential for the initiation of pitting, and indeed it can sometimes occur under conditions of violent impingement.

Condenser Tube Corrosion

Corrosion of condenser tubes was a problem of great magnitude during the first quarter of this century, and the fact that it now occurs but rarely is largely a result of the researches carried out for the British Institute of Metals by Bengough and his collaborators[39, 40, 46], one of whom, May[31, 41, 43], remained associated with the research when it was transferred to the auspices of the British Non-Ferrous Metals Research Association in 1930.

In early times the chief reasons for the failures of condenser tubes were dezincification and impingement attack of the tubes of 70-30 brass or admiralty brass (70 Cu, 29 Zn, 1 Sn) commonly in use. The addition of 0.02 to 0.06 per cent arsenic proved to be an effective inhibitor of dezincification, but failures of these brasses due to impingement attack continued. The development of alloys resistant to this type of attack was a great step forward and immediately reduced the incidence of failures. The two resistant alloys most commonly in use today are aluminum brass (76 Cu, 22 Zn, 2 Al, 0.03 As) and 70-30 cupronickel containing 0.4 to 1 per cent Fe[47, 48, 49, 50]. The former is extensively and successfully used in merchant ships, small naval vessels, power stations, sugar refineries, etc., in condensers where the nominal water speeds through the tubes do not exceed about 8 feet per second (the maximum local velocities being perhaps 2 or 3 times this figure), and where much entangled air is sometimes present. The iron-bearing 70-30 cupronickel has perhaps slightly better all-round corrosion resistance than aluminum brass, and is used in warships, large passenger liners, some power stations, etc. Inhibited 70-30 brass or admiralty brass (70-29-1) is still used for some applications where water speeds are low. In the absence of air bubbles these brasses do not undergo impingement attack until local water speeds reach about 10 to 12 feet per second, but if much air is present severe attack may occur with local speeds as low as 6 feet per second. In ships, particularly warships, considerations of space and weight are of primary importance, and water speeds through condensers are comparatively high, necessitating materials of the highest corrosion resistance. In other applications, however, it is possible to design the condensers so that the conditions are less arduous and in such cases 70-30 or admiralty brass may give satisfactory performance. In some oil refineries, for instance, admiralty brass is preferred because it is said to have better resistance to corrosion by sulfur compounds in the oil products than alloys poorer in zinc, and in these installations the heat exchangers are designed to have low cooling-water speeds, so that corrosion from the sea-water side is not normally troublesome.

Increasing use is being made, particularly in the United States, of condenser tubes of copper-10 per cent nickel alloy containing iron[47, 50a]. Iron contents between about 0.7 and 2.0 per cent have given good results; in general, it appears that the resistance to impingement attack is highest when the iron content is in the upper part of this range, while the resistance to pitting attack in some environments is best when the iron content is lower. Tin bronzes containing 10 to 12 per cent tin have been shown to have good resistance to impingement attack[51, 52] and have been used on a limited scale for condenser tubes. Aluminum bronze tubes have also been found useful in some cases, but in general they appear to be rather susceptible to pitting attack.

The occasional failures which still occur in tubes of normally resistant materials are usually due to one (or sometimes several) of the following factors:

(1) Localized attack or pitting in badly contaminated waters.

(2) Pitting under decaying barnacles, shell fish, or other deposits.

(3) Impingement attack due to extremely high local water velocities at partial obstructions in a tube, *e.g.*, pieces of coke, shell fish, etc.

(4) Erosion due to sand or other abrasive particles suspended in the water.

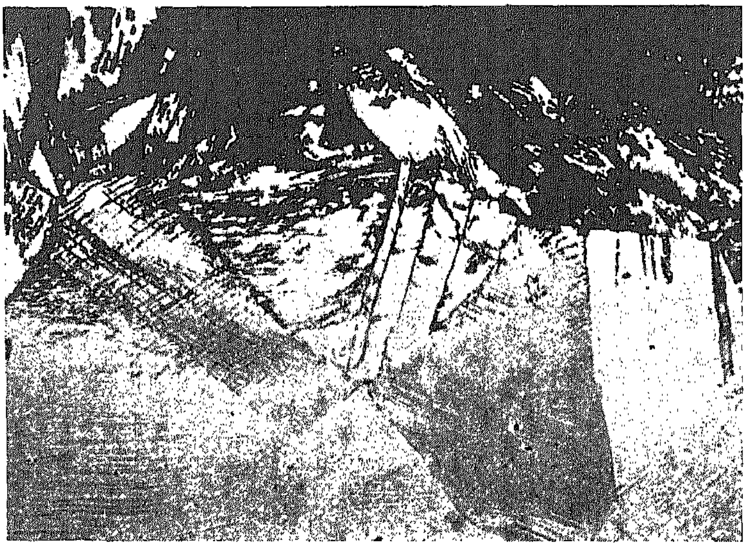

FIGURE 18-3. Penetrative corrosion in 70-30 brass condenser tube used in polluted sea water. Magnification 70X.

(5) Accidental use of wrong materials, or, very rarely, use of materials of incorrect composition or containing manufacturing defects.

The most serious condenser-tube corrosion at the present time arises from the use of polluted cooling waters; in recent years the degree of contamination of many harbors and estuaries has increased markedly. All condenser-tube materials are liable to suffer rapid corrosion in these circumstances, and the choice of materials is made difficult by the fact that different orders of merit apply at different locations. The most satisfactory approach at the present time is to try out a range of materials in the actual condenser in question. The most corrosive waters are those containing free hydrogen sulfide produced by the action of sulfate-reducing bacteria. Figure 18-3 shows severe intercrystalline corrosion produced in a brass condenser tube in such a water. Waters may also be rendered abnormally corrosive by the presence of small amounts of organic sulfur compounds produced by bacterial action, as shown by Rogers[53], who has also described a method of assessing the corrosivity of sea-water samples[54]. In view of these findings corrosion tests performed in synthetic sea waters have limited value.

Other Components in Contact with Sea Water

Tube plates are usually made of 60-40 brass, or preferably naval brass (61-38-1), and although some dezincification may occur this is normally of no consequence in view of the thickness of metal involved. Ferrules, if used, should preferably be of aluminum brass or 70-30 cupronickel. Gunmetal (*e.g.*, 88 copper, 10 tin, 2 zinc) is often used for condenser water boxes of naval ships with excellent results. Monel (usually tinned) is also used for this purpose. Gunmetal, aluminum bronze, phosphor bronze, and various complex brasses are some of the copper alloys used for pump bodies, impellers, valves, etc. working in contact with sea water.

For the main cooling-water trunking of the condenser systems, and for auxiliary services such as fire mains, plumbing systems, etc., copper was formerly used extensively. Under modern conditions, however, its corrosion resistance is often inadequate, impingement attack occurring when the water is moving and pitting when it is stagnant. In British naval ships copper-5 nickel-1.2 iron alloy is now being used for these purposes, possessing considerably better corrosion resistance than copper but similar coppersmithing properties. The development of the copper-nickel-iron alloys by the British Non-Ferrous Metals Research Association has been described by Bailey[47]. In the United States, on the other hand, 70-30 cupronickel has for many years been used for salt-water pipelines in naval ships. It now appears that the copper-10 nickel-1.5 iron alloy will prove an adequate substitute.

The relationship between corrosion and fouling by marine organisms of copper-nickel alloys forms the subject of a paper by LaQue and Clapp[55].

Copper in Fresh Waters

Fresh waters are, in general, less corrosive toward copper than sea water, and copper is widely used for distributing cold and hot waters in domestic and industrial installations. Copper is used for pipes, hot-water cylinders, fire-back boilers, ball floats, etc., and copper alloys for pipes and hot-water cylinders and also for taps, fittings, ball valves, heater sheaths, etc. In condensers and heat exchangers using fresh water for cooling, tubes of 70-30 brass or admiralty brass are usually used, and corrosion is rarely a serious problem.

The types of corrosion which occur in sea water may also occur in fresh waters.

(1) Dezincification of brasses may occur[56] particularly in stagnant or slowly moving warm or hot waters relatively high in chloride and containing little carbonate hardness, so that no protective scale of calcium carbonate is laid down. Dezincification of brasses is inhibited by the usual addition of, for example, 0.03 per cent arsenic (see Figure 18-4), while 1 per cent tin considerably slows down the rate of attack of two-phase brasses. A case of selective corrosion of phosphor bronze has been described[57].

(2) Copper occasionally suffers impingement attack in systems where

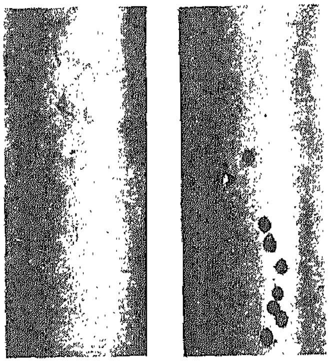

FIGURE 18-4. Brass sheaths of tubular immersion heater after about two years in a soft-water supply. 70-30 brass. Left, 0.02 per cent As, no corrosion. Right, 0.005 per cent As, plugs of dezincification penetrating tube. Actual size.

the speed of water flow is unusually high and the water is one which *does not form a protective film, e.g., a soft water containing appreciable* quantities of free carbon dioxide. Ball-valve seatings may also suffer an erosive type of attack, though sometimes dezincification is the main cause of the trouble. The corrosion of ball valves, including the effect of chlorination of the water, has been studied by Ingleson, Sage, and Wilkinson[58].

Joints in copper components are often a source of trouble. Brazing metal may dezincify; a joint in a copper ball which became leaky by dezincification is shown in Figure 18-5. In some waters soft solders are preferentially attacked, and the safest methods of joining are welding and silver soldering.

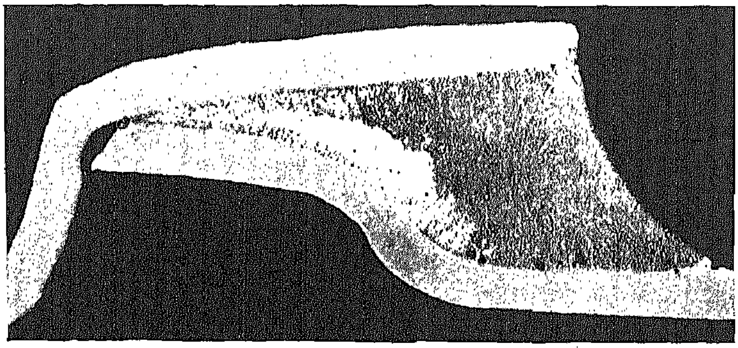

FIGURE 18-5. Dezincification of brazing metal in fresh water, causing leaks in joint of copper ball float. Magnification 15X.

Excessive corrosion of copper is sometimes produced by steam condensates, usually due to the presence of free carbon dioxide.

Two other types of corrosion trouble which deserve special mention are the so-called "green staining," and pitting.

Green Staining. Some waters continuously dissolve appreciable amounts of copper. Factors which favor this action are high free carbon dioxide, chloride, and sulfate contents, low hardness, and increase of temperature. The corrosion is general and the resulting thinning is so slight that the useful life of the pipe or component is virtually unaffected (unless impingement attack occurs). Trouble is therefore confined to (a) stimulation of the corrosion of components of zinc-coated steel[14], light alloys, and sometimes bare steel with which the water subsequently comes into contact; and (b) the formation of green stains in baths, sinks, etc., due to the combination of copper with soaps.

This copper dissolution has been studied by Tronstand and Veimo[59]. Recommendations for water treatment designed to prevent the effect have been given by Kenworthy[60].

Pitting. Occasionally copper water pipes fail by pitting in periods as short as a few months. In Great Britain pitting in the cold appears to be confined to moderately hard or hard waters, usually from deep wells. In the United States deep-well waters are also liable to cause trouble, but in this case the waters are usually soft and high in free carbon dioxide. This problem has been studied by Campbell[61], who has shown that cathodic films which may be produced on the interior surfaces during tube manufacture are primarily responsible for pitting in Great Britain. The dangerous films consist either of carbonaceous material produced during bright annealing operations by the decomposition of residual drawing lubricant, or of a particular type of bright red vitreous cuprous oxide scale. It is presumed that these films provide large surfaces where the cathodic reaction can proceed readily; attack is concentrated at pores and cracks in the film and violent pitting can result. The carbonaceous film becomes wrinkled and cracked as a result of a final hollow-sinking operation.

Failures by pitting are confined to certain districts, and Campbell has shown that in many supply waters in Great Britain pitting cannot proceed even in tubes containing the dangerous cathodic films, owing to the presence in the water of small amounts of a naturally occurring inhibitor, probably an organic colloidal material, which stifles pitting of copper. Trouble therefore only occurs in waters which contain little or none of such inhibitor.

In Campbell's experience pitting in copper hot-water pipes in Great Britain is confined to certain areas supplied with soft waters from moorland gathering grounds. Such failures never occur in less than about seven years, and a feature of the samples examined is the presence of a particular type of scale built up by gradual deposition from the water; this probably functions in a manner rather similar to the carbonaceous films which can lead to cold-water failures. In the United States, however, the situation appears to be rather different and rapid hot-water failures are sometimes experienced.

Atmospheric Corrosion

Copper has a high degree of resistance to atmospheric corrosion, and is widely used for roofing sheets, flashings, gutters, conductor wires, and for other architectural or artistic purposes, *e.g.*, statues and plaques. The good behavior of copper and its alloys is due to the development of protective layers of corrosion products, which reduce the rate of attack. The formation, in the course of time, of the green "patina" gives copper roofs a pleasing appearance which is much admired; indeed efforts have been made to produce it artificially or accelerate its formation[62, 63]. The nature of the corrosion products formed on copper exposed to the atmosphere has been exhaustively studied by Vernon and Whitby[62, 64, 65, 66, 67]. In the early periods of exposure the deposit contains sulfide, oxide, and soot. By the action of sulfuric acid and by the oxidation of sulfide, copper sulfate is formed which hydrolyzes and forms a coherent and adherent basic copper sulfate. Initially this approximates $CuSO_4.Cu(OH)_2$, but gradually increases in basicity until after 70 years or so it becomes $CuSO_4.3Cu(OH)_2$ and is identical with the mineral brochantite. In some cases small quantities of basic carbonate, $CuCO_3.Cu(OH)_2$ (malachite), are also present, and near the seacoast basic chloride $CuCl_2.3Cu(OH)_2$ (atacamite) is produced. Even very near the seacoast, however, sulfate usually predominates over chloride. The presence of atmospheric pollution is thus an essential factor in the development of green patina.

In laboratory tests Vernon[68] has shown that the relative humidity and the presence of sulfur dioxide have a profound effect on the rate of corrosion of copper, as of many other metals. When the relative humidity was less than 63 per cent, there was little attack even in the presence of much sulfur dioxide, but when the relative humidity was raised to 75 per cent, corrosion became severe and increased with the concentration of sulfur dioxide present.

By exposing specimens to the atmosphere at different times of the year, Vernon found that the rate of attack on copper was determined by the conditions prevailing at the time of first exposure. For specimens first exposed in winter there was a linear relationship between increase in weight and time of exposure, indicating that the layer of corrosion product formed under these conditions was nonprotective. For specimens first exposed in summer the square of the increase in weight was proportional to the time of exposure, indicating that the coating formed in summer, when the atmospheric pollution was relatively low, was protective. The parabolic law holds when the corrosion product layer obstructs the access of the corrosive agent to the metal, the rate of attack then being inversely proportional to the thickness of the layer. The protective character of the layer persisted through subsequent periods when the pollution was relatively high.

Copper rapidly tarnishes when exposed to atmospheres containing hydrogen sulfide[69].

Atmospheric corrosion tests on copper and several copper alloys were carried out by Hudson[70] at a number of sites in Great Britain. Corrosion damage was assessed by one or more of the following methods: gain in weight, loss of weight after cleaning, loss of electrical conductivity, and loss of tensile strength. Hudson found that the resistance to atmospheric corrosion was high, and that the rate of attack tended to decrease with time of exposure. Little difference was found between the behavior of arsenical copper and high-conductivity copper, and most of the alloys tested behaved very similarly except for the brasses, which deteriorated more rapidly owing to dezincification.

Tracy, Thompson, and Freeman[71] exposed specimens of eleven different grades of copper in the form of sheet and wire to industrial, marine, and rural atmospheres for periods up to ten years. Differences in the resistance to atmospheric corrosion were found to be small and of little, if any, practical significance. The rate of attack over the ten-year period corresponded to about 4 to 5 $\times 10^{-5}$, 3 to 4 $\times 10^{-5}$, and 2 $\times 10^{-5}$ inches per year for the industrial, marine, and rural atmospheres, respectively.

The American Society for Testing Materials tested copper and nine different copper-base alloys at eight different sites, and the results have been summarized by Tracy[72]. The behavior of all the materials except two of the brasses was in general very similar. Except for these brasses, the rates of attack over a ten-year period, calculated from loss of weight measurements, varied between about 2 $\times 10^{-6}$ inches per year in rural atmospheres to about 9 $\times 10^{-5}$ inches per year in industrial atmospheres. Since the attack is usually very uniform with little tendency to pitting, it is obvious from these figures that copper and most copper alloys exposed to the atmosphere will normally last a very long time, and no protection is usually needed.

Rates of attack up to about 2.5 $\times 10^{-4}$ inches per year were observed for a high-strength two-phase brass in the A.S.T.M. tests. Since the attack was largely by dezincification, however, even this figure gives an inadequate indication of the corrosion damage. Loss of weight or loss of electrical conductivity are unreliable guides to the rate of corrosion for such an alloy, and although the corrosion may not appear serious on visual examination, penetration by dezincification may seriously weaken the material. Thus, in the A.S.T.M. tests the loss in strength was as much as 50 per cent for a high-tensile brass and 30 per cent for a nonarsenical 70-30 brass, while none of the other materials lost more than 10 per cent of their strength during the 10 years' exposure. It is evident, therefore, that it may be unwise to expose some brasses without applying some protection, at any rate in the more corrosive atmospheres.

Unduly rapid corrosion of copper and its alloys in the atmosphere may sometimes occur, usually for one of the following reasons:

(1) An extremely polluted atmosphere such as a railway tunnel.

(2) Bad design or construction, *e.g.*, the presence of crevices where moisture may lodge for long periods.

(3) *Constant dripping of rain water contaminated by atmospheric* pollution (*e.g.*, from nearby chimney stacks) or by organic acids from lichens, etc.

(4) Corrosion-fatigue due to inadequate allowance for expansion and contraction with consequent buckling as the temperature fluctuates.

By attention to design most of these can be avoided.

The special features of corrosion in the tropics have been described by Compton[73].

Soil Corrosion

An extensive series of soil-corrosion tests has been carried out by the National Bureau of Standards in the United States, and the results are given by Logan[74]. Two types of copper and ten copper alloys were exposed in thirteen different soils for nine years. The results for the copper specimens are summarized in Table 18-1.

The behavior of the two types of copper was in general very similar. At the seven least corrosive sites, copper was, with few exceptions, the best material, but most of the alloys lost not more than about twice as much weight, with maximum depths of attack usually not more than two or three times as great as with copper. At the other sites copper was also usually rather better than the alloys, but some of the alloys were occasionally superior.

The two most corrosive sites were rifle peat (pH 2.6) and cinders (pH 8.0). Corrosion of some of the alloys was particularly severe in the cinders. The behavior of the brasses tested, particularly those high in zinc, was rather different from that of the other materials. In most cases dezincification occurred and the brasses were the worst materials.

In the cinders, for instance, several brass specimens were completely destroyed by dezincification. In some of the soils rich in sulfides, however, the brasses were the best materials.

The British Non-Ferrous Metals Research Association has carried out two series of tests the results of which have been given by Gilbert[75] and Gilbert and Porter[76]; these are summarized in Table 18-1. In the first series[75] tough-pitch copper tubes were exposed at seven sites for periods up to ten years. The two most corrosive soils were a wet acid peat (pH 4.2) and a moist acid clay (pH 4.6). In these two soils there was no evidence that the rate of corrosion was decreasing with time of exposure. In the second series[76] phosphorus-deoxidized copper tube and sheet was exposed at five sites for five years. Severe corrosion occurred only in cinders (pH 7.1). In these tests sulfides were found in the corrosion products on some specimens and the presence of sulfate-reducing bacteria at some sites was proved. It is not clear how far the activity of these bacteria is a factor accelerating corrosion of copper, however.

TABLE 18-1. SOIL CORROSION TESTS ON COPPER BY NATIONAL BUREAU OF STANDARDS AND BRITISH NON-FERROUS METALS RESEARCH ASSOCIATION

	Period of exposure, years	Average rate of attack from loss in weight, inches per year	Maximum rate of pitting, mils per year
BNFMRA 1st series: 5 least corrosive soils	10	$0.2 \times 10^{-5} - 1.0 \times 10^{-5}$	Nil
BNFMRA 2nd series: 4 least corrosive soils	5	$2.0 \times 10^{-6} - 9.9 \times 10^{-6}$	1.6
Nat. Bur. Standards: 7 least corrosive soils	9	$1.6 \times 10^{-5} - 9.0 \times 10^{-5}$	1.1
Nat. Bur. Standards: 4 next most corrosive soils	9	$1.0 \times 10^{-4} - 7.8 \times 10^{-4}$	1.8
BNFMRA 1st series: acid clay and acid peat	10	$2.1 \times 10^{-4} - 2.6 \times 10^{-4}$	1.8
BNFMRA 2nd series: cinders	5	2.6×10^{-4}	12.6
Nat. Bur. Standards: rifle peat and cinders	9	$7.3 \times 10^{-4} - 16.7 \times 10^{-4}$	6.4

Cinders and acid peaty soils are obviously two of the most corrosive toward copper. There is, however, no general correlation between the chemical characteristics of soils and their corrosive effects. For instance, in the American tests corrosion in a marshy soil of pH 2.9 was not particularly severe, while the British tests show that high chloride or sulfate contents are not necessarily harmful.

The above tests and general practical experience shows that bare copper can safely be buried in a wide range of soils without fear of excessive corrosion, and in many cases the rate of attack is less than with alternative materials available. There are some situations, however, where the rate of attack is high and protection is necessary if copper is to be buried. Such protection generally takes the form of a bitumen-impregnated wrapping. A tin coating may be beneficial, but cases are known where tinned pipes have failed rapidly due to accelerated attack at scratches and pores. In such cases a bare pipe would probably have lasted longer.

With copper, as with all other buried metals, failures may occur due to stray currents. This does not appear to be a very common cause of trouble, however, probably because copper is usually buried in relatively short lengths and small sizes. Copper alloys are not normally buried, and except in special cases there appears no reason for preferring them to copper. If brass has to be buried the risk of dezincification must be considered and some protection is likely to be desirable. Alpha brasses containing arsenic, which were not tested in the National Bureau of Standards tests, would, however, be expected to be resistant to dezincification.

STRESS CORROSION

Failure of some copper alloys may occur by cracking due to the combined influence of applied or internal stresses and exposure to a corrosive environment. When the stresses are produced by some working operation such as hollow sinking the trouble is usually known as "season cracking." The season cracking of brasses has been extensively studied over the past 30 years or so[77, 78].

It is a feature of the stress corrosion of copper alloys that only certain specific environments appear to produce the effect, notably (a) ammonia or ammonium compounds or related compounds such as amines, and (b) mercury or solutions of mercury salts (which cause deposition of mercury) or other molten metals. The attack produced by mercury appears to be always intercrystalline, but ammonia may produce cracks which are transcrystalline or intercrystalline or a mixture of both, according to circumstances. As an illustration of this, Edmunds[79] found that mercury would not produce cracking in a stressed single crystal of brass, but ammonia did.

The mechanism of stress corrosion of copper alloys is far from completely understood despite the considerable amount of work which has been carried out. Evans[80] suggests that ammonia is effective because it is a feeble corrodant which will produce little attack except at disarranged regions such as grain boundaries or other lattice imperfections and because it will prevent accumulation of copper ions in the crevices so formed due to the formation of stable complexes $[Cu(NH_3)_4]^{++}$. Dix[81] has shown that the cracking of brasses in ammoniacal solution is electrochemical in character and that the grain-boundary regions are strongly anodic, but it has not been established why this is so. Detailed discussions of the mechanism of season cracking have been given by Edmunds[79], by Read, Reed, and Rosenthal[82], and by Chaston[83].

Extensive early work on season cracking of brasses was carried out by Moore, Beckinsale, and Mallinson[84], who found that an acid mercurous nitrate solution was very useful for detecting dangerous internal stresses. This mercurous nitrate test has become widely used as a test for susceptibility to season cracking. Several workers[85, 86, 87] have recently been concerned with the development of standardized tests to measure the probability of cracking in service. Robertson[134] has put forward a theory to account for the effects of mercury on stressed copper alloys.

Stress Corrosion of Brasses

Alloys containing only a few per cent of zinc may fail if the stresses are high and the environment sufficiently corrosive. Most types of brass appear to be susceptible to stress corrosion besides the plain copper-zinc alloys. An extensive investigation of the effect of additions to 70-30 brass was carried out by Wilson, Edmunds, Anderson, and Peirce[88], who found that about 1 per cent silicon was markedly beneficial. Other additions were beneficial under some circumstances and none of the 36 additions tested accelerated stress-corrosion cracking.

In general, the susceptibility to stress corrosion appears to increase with increase in zinc content, but in some circumstances alloys containing 64 to 65 per cent zinc were found to be rather more affected than those containing 70 per cent zinc[89].

The behavior of a wide range of α, $\alpha\beta$, and β brasses in various corrosive environments were studied by Voce and Bailey and the results are summarized by Whitaker[90]. Penetration by mercury and by molten solder was intercrystalline in all three types of brass. In moist ammoniacal atmospheres the penetration of unstressed brasses of all types was intercrystalline. Internal or applied stresses accelerated the intercrystalline penetration of α brasses and initiated some transcrystalline cracking, and also caused severe transcrystalline cracking of β alloys and transcrystalline cracking across the β regions in the two-phase brasses. Immersion in ammonia solution, however, caused intercrystalline cracking of stressed β brasses.

Much work[84, 86, 91] has been done to determine the correct annealing treatments to be applied to brasses to remove internal stresses. Normally a heat treatment at about 275°C (525°F) (a so-called "stress-relief anneal") will lower the internal stresses to a safe value without any appreciable effect on the hardness of the material. It is customary to include in specifications for brass products provision for carrying out a mercurous nitrate test to insure that stresses have been satisfactorily removed, since it is usually impossible to guarantee that the products will not come into contact with a solution or atmosphere containing traces of ammonia or ammonium compounds. Nevertheless service failures still occur from time to time, particularly with components to which stresses are applied in service. In this connection the behavior of the high-strength complex brasses containing up to about 5 per cent aluminum (with small amounts of iron, manganese, tin, etc.) is of interest. These are used for propellers, parts of pumps, nuts and bolts, etc. The $\alpha\beta$ alloys of this type are often used in contact with sea water and usually give good service. Occasional failures by intercrystalline fracture occur, however, and these may be due to stress corrosion caused by traces of ammonia in the environment. Examination of such failures usually reveals thin dezincified layers along the cracks, but it is difficult to decide whether the crack or the dezincification occurred first.

The very high-strength (nearly 110,000 pounds per square inch ultimate tensile strength) β brasses of this type are known to be very prone to intercrystalline failure[92]. In the work described by Whitaker[90] it was found that alloys containing 3 per cent or more aluminum failed with an intercrystalline fracture when stressed at the 0.1 per cent proof stress in an inert environment, indicating an inherent intercrystalline weakness. It was suggested that this might be due to a segregation of aluminum at the grain boundaries. The mechanism of these failures is thus different from the ordinary season cracking of brasses.

Stress Corrosion of Other Copper Alloys

As far as is known pure copper is not liable to undergo stress corrosion[93, 94], but instances are known of the failure apparently by stress corrosion of copper tubes containing about 0.4 per cent arsenic[95] or 0.02 per cent phosphorus[93]. Comparatively little work has been done on the stress corrosion of copper alloys other than brasses, but it appears that failure can occur with aluminum bronzes, tin bronzes, silicon bronzes, and nickel silvers, of certain compositions. All these alloys are much less liable to cracking than brasses, however; the available information has been reviewed by Cook[94].

Thompson and Tracy[93] carried out tests in a moist ammoniacal atmosphere on stressed binary copper alloys containing zinc, phosphorus, arsenic, antimony, silicon, nickel, or aluminum. All these elements gave alloys susceptible to stress corrosion. In the case of zinc the breaking time decreased steadily with increase of zinc content, but with most of the other elements there was a minimum in the curve of content of alloying element against breaking time. In tests carried out at 10,000 psi these minima occurred with about 0.2 per cent phosphorus, 0.2 per cent arsenic, 1 per cent silicon, 5 per cent nickel, and 1 per cent aluminum. In most cases cracks were intercrystalline.

OXIDATION AND SCALING

A number of authors[1, 2, 96, 97, 98, 99, 100] have reviewed the literature on the oxidation and scaling of metals, including copper, or discussed the mechanism of the process. A recent extensive review of information on the oxidation of copper and copper alloys has been given by Tylecote[101], who quotes over 100 references to the literature. Much useful information is given in the book by Kubaschewski and Hopkins[133].

Copper

If during oxidation the ratio of the volume of metal oxide to the volume of metal from which it forms is less than unity, a discontinuous film will form, oxygen reaching the surface via the discontinuities. If the ratio is greater than unity the film initially formed will be compact and continuous, but discontinuities may appear later as a result of thermal or compressive stresses. The ratio for cuprous oxide on copper is 1.7, so that an initially protective film is to be expected. Such a film must grow by a diffusion process and should obey the parabolic law

$$y^2 = Kt + A \qquad (1)$$

(y being the film thickness, t the time, and K and A constants). This has been found to apply for copper in many conditions, but other relationships have been noted. Thus in the very early stages of oxidation a linear growth law has been observed (*e.g.* at 1000°C or 1830°F)[102]:

$$y = Kt \qquad (2)$$

At 180 to 290°C (360 to 550°F) it was found[103] that the parabolic law first applied but subsequently changed to a logarithmic relationship of the type

$$y = K \log B \left(t + \frac{1}{B}\right) \qquad (3)$$

B being a constant.

Other workers have reported a cubic relationship under some conditions:

$$y^3 = Kt + C \qquad (4)$$

C being a constant.

Evans[80, 104] has shown how the effect of internal stresses in growing films may have various effects which can lead to either of the first three growth laws referred to above.

At medium and high temperatures copper ultimately follows the parabolic law[101, 105]. It has been shown[106, 107] using radioactive tracers that the diffusion of copper ions in cuprous oxide is the rate-determining step at 800 to 1000°C (1470 to 1830°F), and there is considerable evidence in favor of the view that metal moves outward through the film by means of vacant sites in the oxide lattice[99, 108]. According to Wagner's theory[100, 109, 110] or developments of it[111] the metal atoms dissociate into ions and electrons, cations and electrons moving outward and anions inward. This would indicate that the resistance to oxidation is closely connected with the electrical resistance of the film.

When oxidation is a diffusion process the oxidation rate should be related to the temperature by the equation

$$K = Ae^{-\frac{Q}{RT}} \tag{5}$$

where K is the rate constant, A a constant, R the gas constant, T the absolute temperature, and Q the activation energy. Values which have been obtained for A and Q are summarized by Tylecote[101]. Pilling and Bedworth[112], Feitknecht[113], and others give values of Q of about 40,000 cal for temperatures of 700 to 1000°C (1290 to 1830°F), while at lower temperatures (up to 500°C or 930°F) Vernon[114] and others obtained values of about 20,000 cal. These values are in agreement with calculations by Valensi[115] based on the assumption that at the high temperatures the oxidation proceeds by the reaction

$$Cu + O_2 \rightarrow Cu_2O \tag{6}$$

while at lower temperatures the rate-determining reaction is

$$Cu_2O + O_2 \rightarrow CuO \tag{7}$$

At low temperatures (*e.g.* 300°C or 570°F) the film consists almost entirely of CuO. As the temperature increases the film consists of a layer of Cu_2O beneath a layer of CuO, the proportion of Cu_2O increasing until at high temperatures the film is almost entirely Cu_2O. The precise composition of the film depends, however, on a number of factors including temperature, time, oxygen concentration in the atmosphere, etc. Tylecote[116] has investigated the composition, properties, and adherence of scales formed on various types of copper at temperatures between 400 and 900°C (750 and 1650°F). At the higher temperatures the scales formed on coppers containing phosphorus were more brittle and less adherent than those formed on coppers containing no phosphorus.

The effects of atmospheres containing hydrogen sulfide have been studied by Dyess and Miley[117] and Vernon[118], and those containing steam and water vapor by Preston and Bircumshaw[119] and Hallowes and Voce[120]. The latter authors also investigated the effects of sulfur dioxide and hydrochloric acid in the atmosphere.

Copper Alloys

With copper alloys containing more noble metals the oxide will be substantially pure copper oxide since the oxides of the noble metals have higher dissociation pressures than the copper oxides. With alloys containing baser metals, however, the alloying element will appear as an oxide in the scale, often in greater concentration than in the alloy itself, and sometimes to the exclusion of copper oxides. The dissociation pressures of many oxides have been calculated by Lustman[98].

Whether the rates of oxidation of an alloy of copper with a baser metal is less or more than that of copper will depend on the concentration of the alloying element and the relative diffusion velocities of metal atoms or ions in the oxide layers. The extensive literature on the oxidation behavior of copper alloys has been summarized by Tylecote[101]. According to Wagner's theory the rate of oxidation will be largely influenced by the electrical conductivity of the film, and the theory is therefore supported by the fact that the alloying elements giving maximum oxidation resistance, beryllium, aluminum, and magnesium, form oxides having very low conductivities, as shown by Price and Thomas[121]. Wagner[109] calculated that when sufficient aluminum was present in copper to cause the formation of an alumina film the oxidation rate should be decreased by a factor of more than 80,000. Experiment showed a factor of only 36, until Price and Thomas[121] carried out initial oxidation under very slightly oxidizing conditions which produced only alumina. On subsequent exposure to full oxidizing conditions, the oxidation rate was decreased by a factor of about 240,000.

Considerable resistance to tarnishing was also obtained by a similar selective oxidation treatment applied to a copper-beryllium alloy. Hallowes and Voce[120] found that selective oxidation of a copper-5 per cent aluminum alloy by Price and Thomas's method protected it from atmospheric oxidation up to 800°C (1470°F) unless the film was scratched or otherwise damaged or the atmosphere contained HCl or SO_2.

Owing to solubility of oxygen some copper-base alloys are liable to develop sub-scales or zones of internal oxidation[122].

Protective Measures

It has been stressed that the good behavior of copper and copper alloys is often dependent upon correct design and choice of material. If proper attention is given to these factors there will usually be no need for protective measures. In special cases, however, *e.g.*, to prevent the dissolution of small amounts of copper or to maintain a high-grade finish, metallic coatings of one or more of the following metals may be applied: tin, lead, nickel, silver, chromium, rhodium, gold. In other cases painting, varnishing, or lacquering may be desirable, or if the conditions are very severe, as in some corrosive soils, heavier protection such as bituminous coating may be necessary. Brasses which are liable to suffer dezincification or stress corrosion may need protection where other copper alloys would be satisfactory unprotected. Occasionally use is made of the principles of cathodic protection, *e.g.*, steel "protector slabs" in condenser water boxes.

The danger of accelerated attack of copper-base materials due to coupling with other metals is small since copper is usually the cathodic member of the couple, but precautions are often necessary to prevent excessive corrosion of the anodic member. Several surveys of the behavior of couples involving copper and copper alloys have been given[5, 6]. One material that has been found capable of accelerating attack on copper in practice is graphite; hence graphitic paints are undesirable. Occasionally the action between different copper-base materials may be appreciable, *e.g.*, gunmetal may stimulate the corrosion of copper or brass in sea water.

The Electrochemistry of Copper

Electrode Potential Relationships

There is some doubt about the precise values of the standard electrode potentials of copper. Determinations of the standard potential of the change

$$Cu \rightarrow Cu^{++} + 2e \qquad (8)$$

lead to a value of + 0.34 ± 0.01 volt at 25°C (standard hydrogen scale)[123]. The standard potential of the change

$$Cu \rightarrow Cu^{+} + e \qquad (9)$$

is more doubtful. Gatty and Spooner[124] prefer the value of + 0.47 volt found by several early workers, but other authors including Pourbaix[125] use the value of + 0.52 volt, which is calculated from the value of the + 0.167 volt found by Fenwick[126] for the reaction

$$Cu^+ \rightarrow Cu^{++} + e \qquad (10)$$

Recently El Wakkad[120a] has deduced a value of + 0.48 ± 0.01 volt. When equilibrium is established between metallic copper immersed in a solution and the two types of ions, a relationship exists between the activities of the two types of ion given by

$$\frac{[Cu^{++}]}{[Cu^+]^2} = K \qquad (11)$$

If the value + 0.52 volt is used for the standard copper-cuprous ion potential, K has the value 1×10^6, but if + 0.47 is used $K = 2 \times 10^4$. Whichever is the true value, in solutions of copper ions in equilibrium with metallic copper, cupric ions greatly predominate (except in very dilute solutions) over cuprous ions.

The change

$$Cu^{++} + Cu \rightleftharpoons 2Cu^+ \qquad (12)$$

will proceed from left to right if the value of K in equation (11) is exceeded and from right to left if it is not exceeded. Cupric ions are therefore normally stable and only become unstable when the cuprous ion concentration is very low. A very low concentration of cuprous ions may be produced, in the presence of a suitable anion, by the formation of either an insoluble cuprous salt or a very stable complex cuprous ion. Cuprous salts can therefore only exist in contact with water if they are very sparingly soluble (*e.g.*, cuprous chloride) or are combined in a complex. Cuprous sulfate can be prepared in nonaqueous conditions, but because it is not sparingly soluble in water it is immediately decomposed by water to copper and cupric sulfate.

The equilibrium between copper and cuprous and cupric ions is disturbed by the presence of oxygen in solution, since reaction (10) is facilitated, the oxygen acting as electron acceptor.

Behavior of Copper Electrodes

The electrode potential behavior of copper in various solutions has been investigated and discussed in considerable detail by Gatty and Spooner[124], but the work can only be referred to briefly here.

A large part of the surface of copper electrodes in aerated aqueous solutions is normally covered with a film of cuprous oxide and the electrode potential is usually close to the cathodic area potential (*i.e.*, the reversible oxygen electrode potential at the existing oxygen concentration and pH, less an overvoltage determined by the cathodic area current density). Principal factors which influence the electrode potential are thus the nature of the solution and the way in which this influences the area of oxide film, and the supply of oxygen to the metal surfaces.

In solutions containing chloride there is a tendency for the establishment of the Cu-CuCl-Cl^- electrode potential, so that the concentration of chloride ions is an important factor in determining the electrode behavior. From a knowledge of the solubility products of cuprous chloride and cuprous oxide it is possible to predict under what conditions chloride or hydroxide ions are the potential-determining ions. According to Gatty and Spooner, chloride determines the potential if $[OH^-] < 10^{-8.1} \times [Cl^-]$ and hydroxide if $[OH^-] > 10^{-8.1} \times [Cl^-]$. This will not hold in concentrated solutions, however, since complex $CuCl_2^-$ ions will be present as well as simple ions. A further factor to be considered is the ready formation of insoluble basic compounds. In solutions not containing chloride (*e.g.*, sulfate or nitrate solutions), corrosion rates are usually lower and the electrode potential is more steady over a wide range of conditions. In this case Gatty and Spooner consider that the rate of corrosion is probably determined by the rate at which metal ions can escape through pores in the protective oxide film, and this is supported by the results of experiments on the anodic and cathodic polarization of copper. The effect of oxide films on the electrode potential of copper has also been studied by Tourky and El Wakkad[127].

Pourbaix has developed a general method, based on generalized thermodynamic equations, for the calculation of equilibrium conditions in dilute aqueous solutions, and in particular has developed a method of representing such equilibria graphically, so that a great deal of useful information is given in a small space. Such diagrams have been given by Pourbaix[125] for the systems Cu-H_2O and Cu-Cl-H_2O. Within potential-pH ordinates it is possible to indicate domains where the metal is (a) immune from attack because its potential is so depressed as to prevent dissolution (*e.g.*, as in cathodic protection); (b) able to corrode freely; and (c) liable to become passivated by the formation of films of insoluble corrosion products.

One of Pourbaix's diagrams is shown in Figure 18-6. Such a diagram is of considerable assistance in discussing many problems related to the chemistry, electrochemistry, electrodeposition, and corrosion of copper. It is well recognized, of course, that the thermodynamic approach has limitations, the most important of which is that, though predictions can be made about the possibility of a given reaction proceeding in certain circumstances, no information can normally be gained about the rate at which it will proceed if it can.

A study of the behavior of copper when anodically polarized has been made by Hickling and Taylor[128] using an oscillographic method which

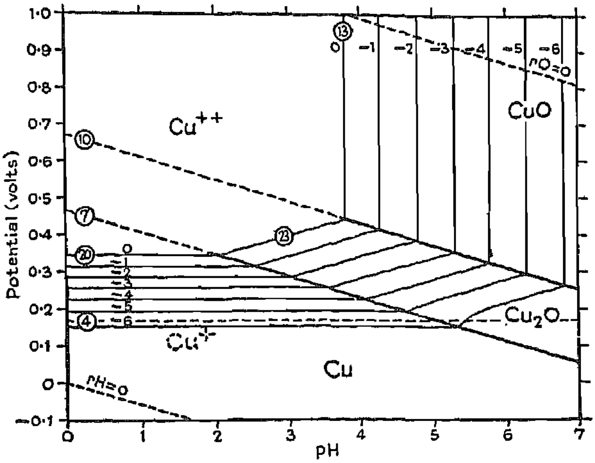

FIGURE 18-6. Potential-pH equilibrium diagram, system Cu-H_2O. (From M. J. N. Pourbaix, "Thermodynamics of Dilute Aqueous Solutions," London, Edward Arnold & Co., 1949, by permission.)

records the variation of potential with quantity of electricity passed. In alkaline solutions the main stages of polarization were (a) the charging of a double layer, and (b) the formation of a film of cuprous oxide which was almost at once oxidized to cupric oxide. In 0.1 *N* NaOH the film was about four molecules thick when oxygen evolution first commenced. In buffer solutions of decreasing pH, the formation of sparingly soluble salts preceded or accompanied the formation of the oxide film and in acid solutions giving soluble copper salts no passivity developed, the anodic process being just dissolution of copper. Other workers have also studied the anodic behavior of copper in alkaline[129] and in acid[130] solutions.

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Chapter 19

The Effect of Impurities in Copper

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In the process of electrolytic refining the impurities in the anodes either dissolve in the electrolyte or form slimes. Minor mechanical occlusions of both during the deposition of the cathodes are inevitable, resulting in the presence of traces of Ag, Au, As, Sb, Bi, Sn, Pb, Fe, Ni, Se, Te, and S in refined copper. Except for Fe, S, and O_2, which are altered and controlled during the final melting operation, the quantities of the impurities in the finished product reflect the operational methods of the producing refineries and the relative composition of the blisters being treated.

Ordinarily, electrolytic refining lowers the concentration of any individual metallic impurity to a maximum of 0.002 per cent; their total is usually less than 0.01 per cent and some impurities are present only in the fourth or fifth decimal place. Fire refining permits a limited removal of Se and Te, and is practically ineffective with respect to Ag, Ni, and Bi; the impurity content of any fire-refined copper, therefore, is much more closely related to the composition of the blister source than is electrolytic copper.

Electrical Conductivity

All impurities lower the conductivity of copper[1, 2, 3], but fortunately the potent offenders are limited to those elements which enter into solid solution in the metal. Impurities which form sufficiently stable insoluble oxides, such as Fe, Sn, and Pb, are precipitated in inert form in tough-pitch copper, and thereby lose their effectiveness. (Oxides of such elements as Zn, P, Co, Cr, Si, and Al are similarly formed, but these elements are usually eliminated during refining). Sb and Cd also form oxides, but they are unstable above 700°C (1290°F) and commercial processing methods ordinarily do not provide sufficient time at favorable reaction temperatures for complete precipitation to occur, so that for practical purposes they should be classed as being partially effective in tough-pitch copper. Bi apparently behaves in a similar manner, but has little effect on conductivity. The magnitude of the beneficial effect of oxygen is best illustrated by a comparison of Figures 19-1 and 19-2, which indicate the reduction of conductivity in both oxygen-bearing and oxygen-free copper caused by each individual impurity[4, 5]. These individual effects are arithmetically added to obtain the total effect of all the impurities present in any refined copper.

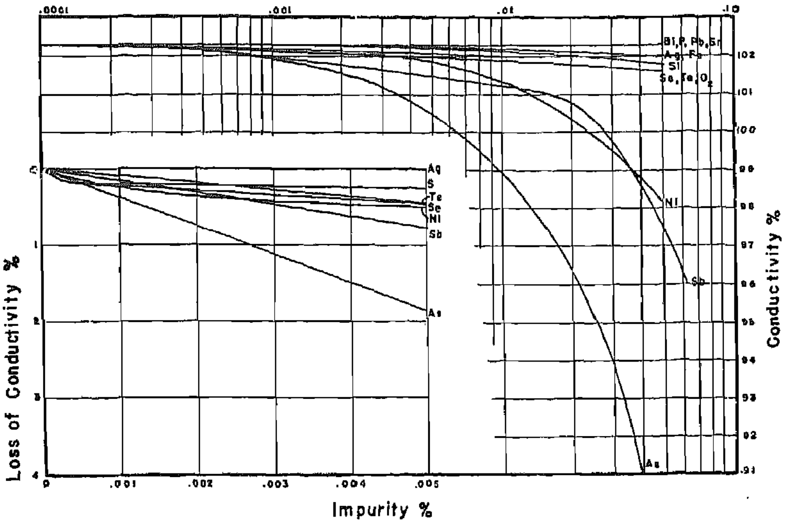

Figure 19-1. Decrease of conductivity of tough-pitch copper with content of impurities.

Precipitated phases, while inert, do displace an equivalent volume of copper. The loss of conductivity from this source is comparatively small, but it becomes measurable when a foreign element is present to the extent of 0.010 per cent. For each 0.01 per cent oxygen, for instance, the Cu_2O formed will lower the conductivity by 0.136 per cent.

Impurities such as Ag, As, Ni, Se, Te, and S (in amounts below 0.05 per cent) do not form stable oxides and therefore can affect the conductivity of copper, regardless of oxygen content. Of these elements, Ag has only a small influence and the potential effects of Se, Te, and S are greatly restricted because of their limited solubilities in solid copper. Since these solubilities increase appreciably at hot-working temperatures, it is important to recognize that rapid cooling or quenching from above 650°C (1200°F) will result in an increase in the effectiveness of these impurities on both the conductivity and the annealing temperature.

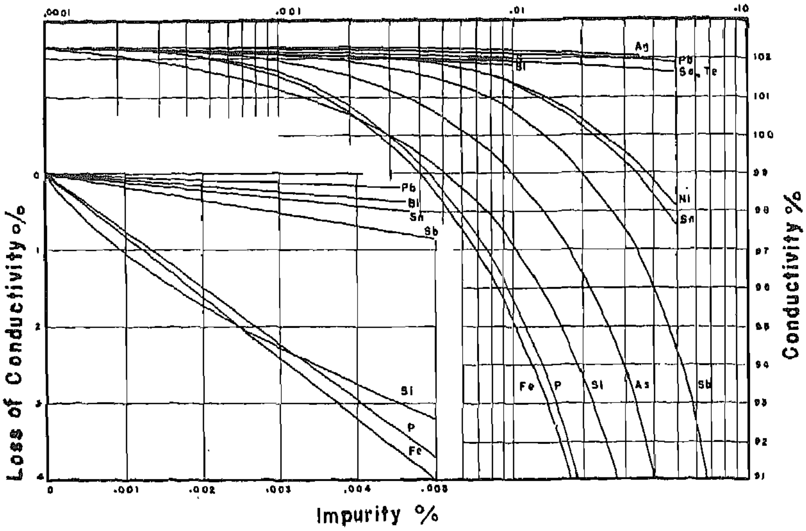

FIGURE 19-2. Decrease of conductivity of oxygen-free copper with content of impurities.

Annealing Properties

Unlike conductivity, the softening temperature of cold-worked copper can be increased by both soluble impurities and certain precipitated phases, although most oxides are inert. In addition, the total increase in softening temperature is not the arithmetical sum of the individual impurity effects, and in many instances it is only slightly more than the effect of the element present having the greatest individual influence.

High-purity copper, cold worked 75 per cent, will reach the half-hard stage of the annealing curve when annealed for one hour at 140°C (284°F), whereas the equivalent softening temperature for commercial ETP copper generally falls within the range 175 to 225°C (345 to 435°F). While the variations in impurity content responsible for the existence of this range of properties in the commercial product are well within normal refinery tolerances, a somewhat conflicting demand exists for copper having very low annealing properties to satisfy such marginal annealing operations as are simultaneously carried out in baking the coatings of insulated wire. As described previously, these differences are due not only to basic impurity contents, but also to any increase in solid solubility that has been permitted by the thermal details of the fabricating procedure. Quenching rolled rods from temperatures above 650°C (1200°F) will increase the softening temperature of the wire fabricated from them. Conversely, slow cooling or annealing in the precipitation range of 500 to 600°C (930 to 1110°F) will have the opposite effect.

In the oxygen-free condition (with the exception of coalesced copper), the softening temperature is normally higher since the possibility of formation of impurity oxides is removed. However, where sufficiently high annealing temperatures are required to permit soldering operations or service at elevated temperatures without undue softening, it is usually necessary to add an element for the purpose. As can be seen from Table 19-1, phosphorus, which is widely used as a deoxidizer, is sufficiently effective to satisfy many such requirements, particularly where they refer to tubing. If high conductivity must be maintained, and tough-pitch copper is to be used, sufficient silver is normally added to accomplish the desired result.

TABLE 19-1. SOFTENING TEMPERATURE (DEG. C) OF PURE COPPER CONTAINING INDIVIDUAL IMPURITY ADDITIONS

(Samples Annealed ½ Hr. at 600°C (1110°F) Prior to Final Cold Reduction of 75 Per Cent.)
Softening Temperature of Pure Copper = 140°C (284°F)

Quantity	0.002%		0.005%		0.01%		0.05%	
Impurity	T.P.[a]	O_2-free	T.P.	O_2-free	T.P.	O_2-free	T.P.	O_2-free
O_2	140	140	140	140	140	140	140	140
Fe	140	146	140	153	140	155	148	167
Sb*	180	192	258	282	296	317	336	336
As	168	168	189	189	205	205	242	242
Ni	140	140	140	140	140	140	140	140
Pb*	146	250	146	270	146	274	146	286
Bi*	210	260	247	300	275	328	......	......
Ag	148	148	172	172	207	207	330	330
Sn	140	198	140	277	140	315	140	346
S**	181	181	183	183	183	183	......	......
Se**	222	222	234	234	240	240	250	250
Te**	212	212	228	228	238	238	250	250
P	140	258	140	284	140	300	......	......
Si	......	161	......	181	......	198	......	242
Co	......	145	......	152	......	161	......	161
Cr	......	152	......	190	......	260	......	320
Zn	......	148	......	151	......	152	......	156
Cd*	......	183	......	248	275	309	325	356

[a] Copper containing oxygen in the tough-pitch range.
* Tough-pitch values reflect partial oxide formation. Values equivalent to those given for oxygen-free copper can be obtained by heat treatment at temperatures in excess of 700°C (1290°F).
** Much higher values obtainable by heat treatment to increase solid solubility.
Data from references 4, 5, and 6.

Grain Growth

Grain growth in high-purity copper occurs readily at increasing annealing temperatures, but the average grain size produced is usually rather nonuniform. Commercially refined coppers may behave quite differently due to the presence of precipitated phases, some of which are extremely effective in inhibiting grain growth. Thus, in tough-pitch copper (and coppers that contain at least the limit of solid solubility of oxygen at 850°C, 1560°F) only a very limited amount of grain growth occurs within the normal annealing range, due to the restrictive effects of Cu_2O[6, 7].

Since deoxidized and oxygen-free coppers are relatively free from this influence, they behave more like high-purity copper, and the presence of minor amounts of impurity precipitates actually tends to produce a more uniform grain size than would otherwise result. Accordingly, various annealed tempers can be achieved with these types in commercial annealing practice, although the degree of control is hardly equivalent to that obtainable with brass.

This behavior is valid only for products which are deoxidized by methods normal to present commercial practice. If such material is remelted and solidified under extraordinary reducing conditions, such as may be achieved by prolonged contact of the molten metal within a closed graphite system, grain growth may be almost completely inhibited even at annealing temperatures in excess of 800°C (1470°F), depending on the degree of deoxidation obtained. This type of restriction does not occur in sulfur-free copper, and does not appear to be influenced by the other common impurities when present in normal amounts. However, the effect is readily produced by the presence of as little as 0.0003 per cent S, a minimum which all commercial coppers exceed[6].

Another type of inhibition that can be circumvented by control of the processing technique is that due to the texture produced by very severe cold working*. All of these restricting effects behave similarly to the extent that they require the use of such high annealing temperatures to initiate appreciable grain growth that a nonuniform process results which usually produces a mixture of fine and exceedingly coarse grains. Whether a restricting effect is present or not, a much more precise control of the grain size of copper can be obtained by regulation of the final reduction so as to base the desired increase or decrease primarily on the recrystallized grain size, without resort to grain growth.

Hot and Cold Working

In the foregoing, the behavior of impurities has been described in terms of those effects that are important to the daily fabrication and end use of the relatively pure electrolytic copper of commerce. With copper of such purity, the hot-working characteristics are so excellent that quality-control measures are almost entirely confined to the insurance of good casting and fabrication practices. In like manner, the presence or absence of Cu_2O *is more important to cold-working methods than the* minor variations of impurities encountered between the products of different refineries.

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* Summarized in Reference 7.

This situation does not hold for fire-refined coppers, which must be evaluated in terms of the impurities peculiar to each brand.

The effects of the individual elements are closely related to their solubilities and tendencies to form compounds, and can be considered by groups of like characteristics.

(1) Ag, Au, Ni, and As are soluble irrespective of oxygen content when present as impurities. Since no soluble impurity has been found to be deleterious to the hot workability, these elements are regarded as innocuous. In greater amounts, Ni and As form oxides[3], in quantities which are small compared to the amounts in solid solution, and the resulting effects are considered to be of minor importance.

(2) Cd and Sb behave similarly to the above group, except that partial precipitation as oxide can occur in the impurity range below 700°C (1290°F)[5]. Hot- and cold-working operations are readily carried out in the presence of many times the quantity normally occurring in the impurity range, although antimony should not exceed 0.4 per cent in oxygen-free or 0.5 per cent in tough-pitch copper[14].

(3) Fe, Sn, Zn, P, Si, and Al are also soluble, but in the presence of oxygen form stable oxides having relatively high melting points. In either case they do not impair hot or cold workability significantly, since in the soluble condition they form ductile alloys, and in the oxidized form they separate rapidly from the molten metal, and are difficult to entrain in harmful quantities.

(4) Se, Te, S, and O_2 form compounds of the general form Cu_2X. Such phases are essentially brittle, and decrease both hot and cold workability gradually as their quantity increases. Hanson, Marryat, and Ford have estimated that at least 0.36 per cent O_2 can be tolerated for hot working, but this amount would be cause for serious complaint during commercial cold-working operations[8, 3]. Consequently, most tough-pitch copper does not contain more than approximately 0.06 per cent O_2. High amounts of sulfur are virtually unknown due to casting difficulties. Selenium and tellurium additions of 0.5 per cent are made for their free-machining effects, but a distinct loss of fabricating properties results which, as in the case of oxygen, is more noticeable in cold-working operations than at elevated temperatures.

(5) Bi and Pb also form ductile solutions, but their solubilities are so limited that precipitation occurs within the impurity range. In oxygen-free copper molten Bi and Pb separate as the temperature falls during hot working, resulting in extreme brittleness. Since the solid solubility of Bi and Pb at 800°C (1470°F) is about 0.01 per cent[9] and 0.04 per cent[6], respectively, and becomes almost negligible at 500°C (930°F), serious difficulties are experienced in hot working oxygen-free material unless it contains considerably less than these solubility limits.

Bismuth is especially deleterious because it occurs in the form of films at the grain boundaries[3, 10]. Probably its embrittling effects are closely related to the development of these films, which depend on other factors such as grain size and thermal history as well as Bi content[9], but it would appear that the practical limit of Bi in oxygen-free copper is about 0.002 per cent. Additions of P, Cd, and Sn[11, 12, 13] are known to improve materially the workability of coppers containing Bi. Inasmuch as Pb separates in the form of globules its safe limit in oxygen-free copper is somewhat higher, approximately 0.02 per cent[3]. Such limits are, of course, not absolute; rather they represent some degree of entrance into the troublesome range.

In the presence of oxygen, both Bi and Pb form oxides below 700°C (1290°F)[3]; the reaction is reversible at higher temperatures as in the case of Sb and Cd. Consequently, as the temperature decreases during hot working the separation of injurious metallic impurity is avoided by the reaction forming a much less harmful oxide. Tough-pitch coppers can be rolled with far greater amounts of Bi and Pb than can be tolerated in the oxygen-free condition, but as a general rule, it is doubtful whether the above limits should be more than doubled in practice.

Both of these impurities impair the cold-working properties, and in fact, by proper manipulation of heat treatment, it is quite possible to hot work a copper containing Bi, and produce a very brittle product that would be useless for cold reduction. However, the limits previously given for hot working are considered to be within the established tolerances for cold working as well.

From the general behavior of the solubility increases of those impurities which offset hot workability, it is quite understandable that the more impure coppers should be worked at the highest possible temperatures. This has been fully demonstrated in practice, and is generally applied to the fabrication of many fire-refined coppers. In addition to the effects already described, there are many specialized details relating to the influence the impurities in such coppers have on their commercial applications which cannot be satisfactorily treated in a general discussion.

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Chapter 20

The Physical Chemistry of Copper

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Copper, atomic number 29, is the first element of the subgroup IB of the periodic table. The other members of this subgroup, with very similar properties, are silver and gold. These elements are characterized by being not very reactive chemically, the activity decreasing as the atomic number increases. They are toward the noble end of the electrochemical series, and are electronegative to hydrogen.

The electronic structure of the free atom of copper is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$. The $4s$ electron has a low ionization potential, and is easily removed to give the cuprous ion Cu^+. The ionization potential for the removal of one electron from the $3d$ shell is, however, only slightly higher. As a result, a cupric ion, Cu^{++}, is easily formed. In metallic structures it is usually considered that copper is only singly ionized, so that the $3d$ electrons do not enter into the bonding.

The crystal structure of copper is face-centered cubic, the cube side being 3.6078Å at 18°C, and the closest distance of approach of atoms 2.551Å. This is a close-packed structure, being one of the two possible structures formed by the closest possible packing of uniform spheres. The closest-packed planes are the octahedral {111} planes; the closest-packed directions are the <100> directions. Each atom has twelve equidistant nearest neighbors. The structure has the highest degree of atomic concentration and symmetry to be found in any crystal structure.

MODE OF DEFORMATION

Although the working of copper is dealt with elsewhere in this volume, it is perhaps useful to summarize here the fundamentals of the mode of deformation of copper.

There has perhaps been less work on single crystals of copper than on other face-centered cubic metals, but the general picture is clear. Plastic flow of copper single crystals commences by the classical process of slip. In common with other metals of face-centered cubic crystal structure, slip occurs on the close-packed {111} planes in the close-packed <100> directions. As there are four such {111} planes, with three <100> directions in each plane, there are twelve possible systems on which slip may occur. The slip system which operates is that in which *the resolved shear stress on the slip plane in the slip direction is a maximum*, as was originally demonstrated by Taylor and Elam[1]. With single crystals in tension, this occurs for slip planes making an angle of approximately 45° with the tension axis. If only one such system is favorably oriented, then once the shear stress along this direction and plane has exceeded a critical value, deformation commences by slip on this single system. Where more than one system is favorably oriented, slip will occur simultaneously on these systems. Slip does not occur on all possible planes of one slip system, but is concentrated on relatively few slip planes, giving rise to the familiar slip lines on the surface of deformed specimens.

The critical resolved shear stress depends on the purity of copper used, and on the treatment and handling of the crystal; but Brandenburger[2] gives a value of 0.10 kg per sq mm for copper single crystals.

The actual tensile stress required to give this resolved shear stress, and thus initiate slip, will depend on the orientation of the crystal planes to the tension axis; but with the large number of slip systems possible for copper, the maximum tensile stress can only vary by a factor of two. In hexagonal metals such as zinc, with only three possible slip directions and a single slip plane, the variation is much greater. This multiplicity of slip systems is a partial explanation of the greater capacity for cold work of copper as compared with metals such as zinc and cadmium.

Prior deformation increases the shear stress necessary to cause slip to recommence, and this is particularly marked for copper, as Schmidt and Boas[3] have shown. During single slip the crystal orientation rotates; a point is reached at which another slip system is also favorably oriented for slip, and duplex slip then occurs.

This picture is rather oversimplified in presenting slip as first slip on a single system, then slip on two systems. More detailed recent work shows that after only a small amount of deformation the slip process becomes complex. Little of this work has been done using copper, but work on copper by Mathewson[4], and in this laboratory[5], gives results in general agreement with work on other face-centered-cubic metals. The picture is complex, but other slip systems and modes of deformation enter, notably those designated "cross-slip" and "kink bands." There has been rather more work of this type on crystals of α brass[6, 7], for which similar observations were made.

Due to the rotation of crystal orientation during slip, the working of polycrystalline specimens results in the production of a preferred orientation of the axes of the individual crystals. Only a summary of the preferred orientations produced by various methods of working will be given here. This summary was made by Boas[8].

Rolling: [110] plane parallel to rolling plane, [112] direction parallel to rolling direction.

Drawing: [111] and [100] directions parallel to wire axis (double fiber structure).

Compression: [110] direction parallel to compression axis.

Torsion: [111] direction parallel to torsion axis.

It should be noted that these are ideal textures; actual results show a scatter of orientation from these ideal positions, and should properly be expressed as pole figures.

DIFFUSION

It is not possible here to give even a brief account of modern diffusion theory, and up-to-date reviews of the subject are available[9, 10]. The experimental facts, however, can conveniently be summarized, to a good degree of approximation, by various semi-empirical equations. The usual definition of diffusion coefficient is derived from Fick's first law, one form being:

$$S = -AD\frac{\delta c}{\delta x}$$

where S is the amount of material diffusing in unit time through area A, perpendicular to the x axis at a point where the concentration gradient is $\frac{\delta c}{\delta x}$. D is the diffusion coefficient. The negative sign indicates that the diffusion occurs down the concentration gradient.

The variation of D with temperature, over a limited temperature range, can usually be expressed to a good degree of approximation by:

$$D = D_0 e^{-E/RT}$$

D_0 has the same dimensions as D and is independent of temperature (so far as this equation holds). E is the activation energy for diffusion, usually expressed in kg cal per gram atom, R is the gas constant, T the absolute temperature, and e the exponential function.

D may vary with concentration, and under these circumstances D_0 and E also usually depend on concentration.

In polycrystalline material diffusion can occur through the lattice, over the surface, or along grain boundaries. There are only a few data available on these three modes of diffusion in any one system, but it appears that in general the activation energies E for the various modes are, in magnitude,

$$E_{\text{surface}} < E_{\text{grain boundary}} < E_{\text{volume}}$$

Since the activation energy is generally the major factor in determining diffusion rate at temperatures at which diffusion is appreciable, it follows that

$$D_{\text{surface}} > D_{\text{grain boundary}} > D_{\text{volume}}$$

In some cases, in fact, the total amount of solute diffusing along grain boundaries may exceed the amount diffusing through the grains, despite the much larger number of available paths for volume diffusion than grain-boundary diffusion. In most investigations no distinction has been made between the various modes of diffusion; this applies to the data of Table 20-1.

Table 20-1 summarizes a large number of results on diffusion in copper-base alloys, and is adapted from Smithells[11]. This gives the constants of the second equation above. The column headed Concentration indicates the composition for which the diffusion constants appear to be valid; where these have been calculated for a definite composition the entry is in **heavy type.** Where the experimental conditions are less well-defined a value of concentration is given in ordinary type. A number of the results are presented graphically in Figures 20-1, 20-2[15], and 20-3[17].

In a recent investigation of diffusion in ternary alloys of copper[24], it was shown that small additions of a third element affected the rate of diffusion of zinc in brass; the change in activation energy E was proportional to the valency of the added third element.

ALLOYING BEHAVIOR OF COPPER

The systematic study of the factors which determine the alloying behavior of metals has not yet reached the state at which quantitative prediction of the features of an unknown phase diagram is possible. However, a number of the more prominent factors are known, and their influence can be discussed in at least a qualitative manner. It is not possible to give a detailed treatment here of these factors, or of their basis in atomic theory; for a more thorough treatment the reader is referred to references 25, 26, and 27. The alloying behavior of copper can, however, be conveniently discussed in terms of these factors.

Solid Solutions

The Effect of Atomic Size. One important influence is that of atomic size. The size of an atom is difficult to define to a high degree of precision,

TABLE 20-1. THE DIFFUSION OF VARIOUS ELEMENTS IN COPPER

Diffusing metal	Concentration (atomic per cent)	Temperature °C	D (cm²/sec)	D_0 (cm²/sec)	E (kg cal)	Ref.
Cu, self-diffusion		650	3.2×10^{-12}	—	—	12, 13
		850	$0.8\text{-}2.6 \times 10^{-10}$			
		1030	2.8×10^{-9}	47.0	61.4	14
Al	0.8	800	See Figs. 20-1 and 20-2	1.75×10^{-2}	37.7	15
	4			4.55×10^{-2}	39.5	
	8			3.75×10^{-1}	43	
	12			6.76	48	
	16			2.53×10^{2}	54	
Au	Multiple layers Au-Cu	20	5.0×10^{-20}	—	—	16
Be	0	800	See Figs. 20-1 and 20-2	2.32×10^{-4}	28	15
	4			7.13×10^{-4}	30	
	8			3.18×10^{-2}	37	
Cd	0	800	0.8×10^{-10}	1.97×10^{-9}	8	15
	0.5		1.5×10^{-10}	1.97×10^{-8}	10	
Mn	8-11.4	400	2.0×10^{-13}	0.72×10^{-5}	23.2	17
		650	3.7×10^{-11}			
		850	1.3×10^{-10}			
Ni	7.5-11.8	550	7.1×10^{-13}	6.5×10^{-5}	29.8	17
		700	1.4×10^{-11}			
		950	2.1×10^{-10}			
			See Fig. 20-3			18
Pd	4.3-6.2	490	9.0×10^{-13}	0.16×10^{-5}	21.9	17
		700	1.3×10^{-11}			
		950	2.5×10^{-10}			
Pt	2.4-3.5	490	5.8×10^{-13}	1.02×10^{-4}	21.9	17
		700	1.3×10^{-11}			
		950	$1.10\text{-}2.32 \times 10^{-10}$			
Si	0	800	See Figs. 20-1 and 20-2	3.7×10^{-2}	40.0	15
	4			4.06×10^{-1}	48.2	
	8			18.6	53.8	
Sn	0	800	See Figs. 20-1 and 20-2	1.13	45	15
	4			3.25×10^{-3}	30.5	
	5.6-8.0	475	1.8×10^{-11}	—	26	19
		600	$2.1\text{-}2.8 \times 10^{-10}$			
		708	8.7×10^{-10}			
Zn	0-18	800	See Figs. 20-1 and 20-2	—	—	15
	0-9.25	641	5.1×10^{-14}	5.8×10^{-4}	42.0	20
		884	6.4×10^{-12}			
	0-28.6	641	2.3×10^{-13}	3.2×10^{-3}	42.0	20
		884	3.4×10^{-11}			
	27.5-35.4	700	0.6×10^{-7}	—	24.5	21, 22
		950	1.44×10^{-6}			
	α brass	800	From $1.2\text{-}3.1 \times 10^{-8}$	—	—	23
	β brass	800	From $1.16\text{-}1.39 \times 10^{-7}$	—	—	23

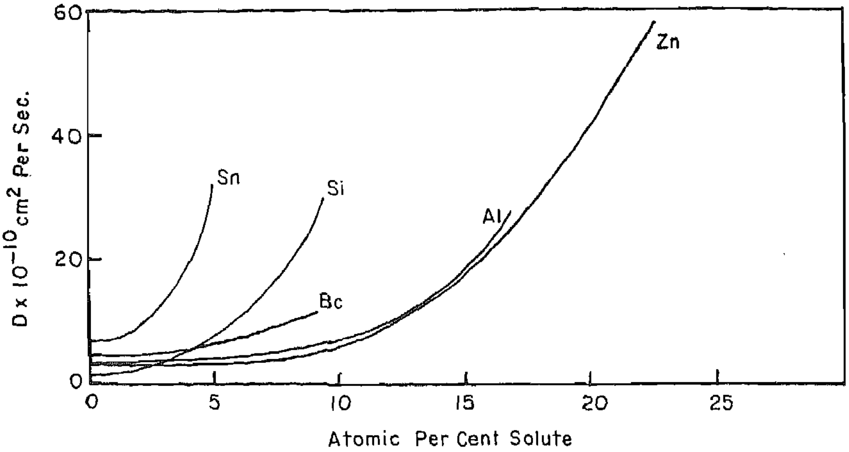

FIGURE 20-1. Diffusion coefficients, *D*, for diffusion in solid solutions of various elements in copper at 800°C[15].

and, indeed, it is certain that the effective size of an atom depends on the structure in which it is present. To a first approximation, and when dealing with metallic types of structure, the atomic size can be taken as constant. The most convenient measure of the atomic size in metallic structures is an "atomic diameter," defined as the closest distance of approach of atoms in the crystal structure of the element; that is, as if the atoms were spheres of uniform diameter in contact at their nearest

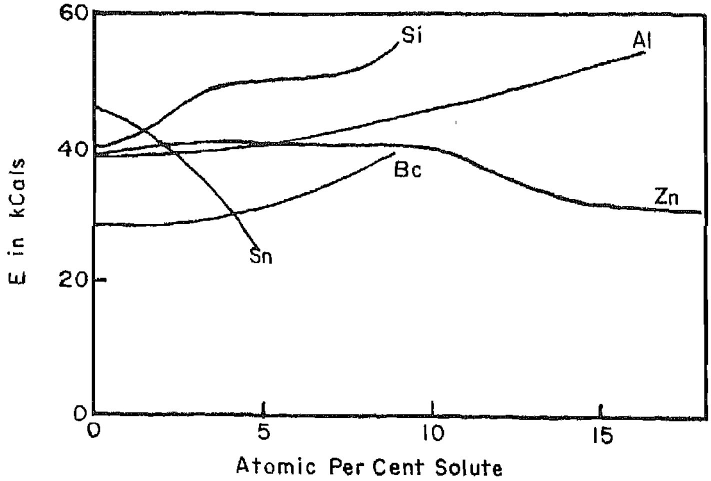

FIGURE 20-2. Activation energies for diffusion in solid solutions of various elements in copper[15].

approach. This definition is arbitrary, but adequate for many discussions. Many refinements have been suggested, and some will be mentioned later.

It was first proposed by Hume-Rothery, Mabbott, and Channel-Evans[28] that primary substitutional solid solutions were very restricted when the size of solvent and solute atoms, defined in this way, differed by more than 14 to 15 per cent. Figure 20-4 shows the atomic diameters of the elements, defined as above, and two parallel lines have been drawn at a distance of 0.35Å from this value, *i.e.,* 14 per cent. Between these limits the size factor is said to be favorable, and wide solid solutions may be formed if other factors permit. Thus, with the divalent elements of Group II, there are wide solid solutions of beryllium (16.6 atomic per cent) and zinc (38.4 atomic per cent) in copper, where the size factors are favorable; but restricted solutions of cadmium (1.7 atomic per cent) and mercury (uncertain, small), where the size factor is unfavorable. Wide solid solutions are not necessarily always formed where the size factor is favorable, for other factors influence the extent of solid solution. This size-factor rule can best be used as an initial guide in deciding whether an element is likely to show extensive solid solubility or not.

The zone of favorable size factor, a difference of 14 per cent in diameters, is arbitrary, and if the atomic diameter is near the limit of favorable size the results tend to be erratic. It is particularly in such cases that more refined definitions of atomic size are probably necessary.

It is worthy of note that in the majority of such borderline cases,

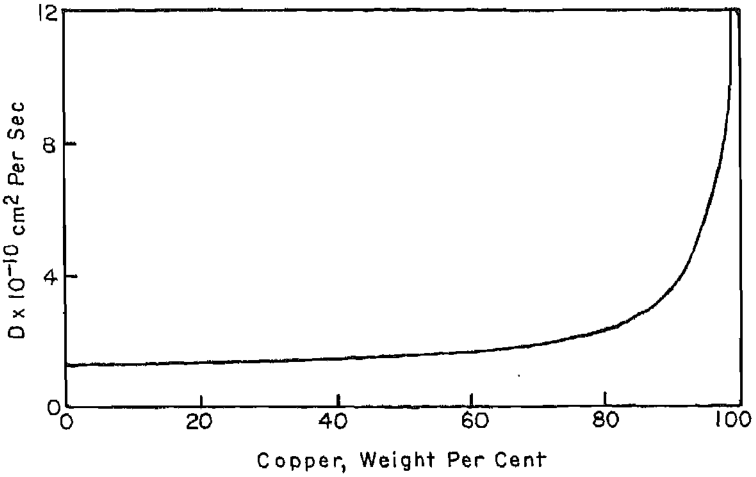

FIGURE 20-3. Diffusion coefficients for copper-nickel alloys at 1025° C[17].

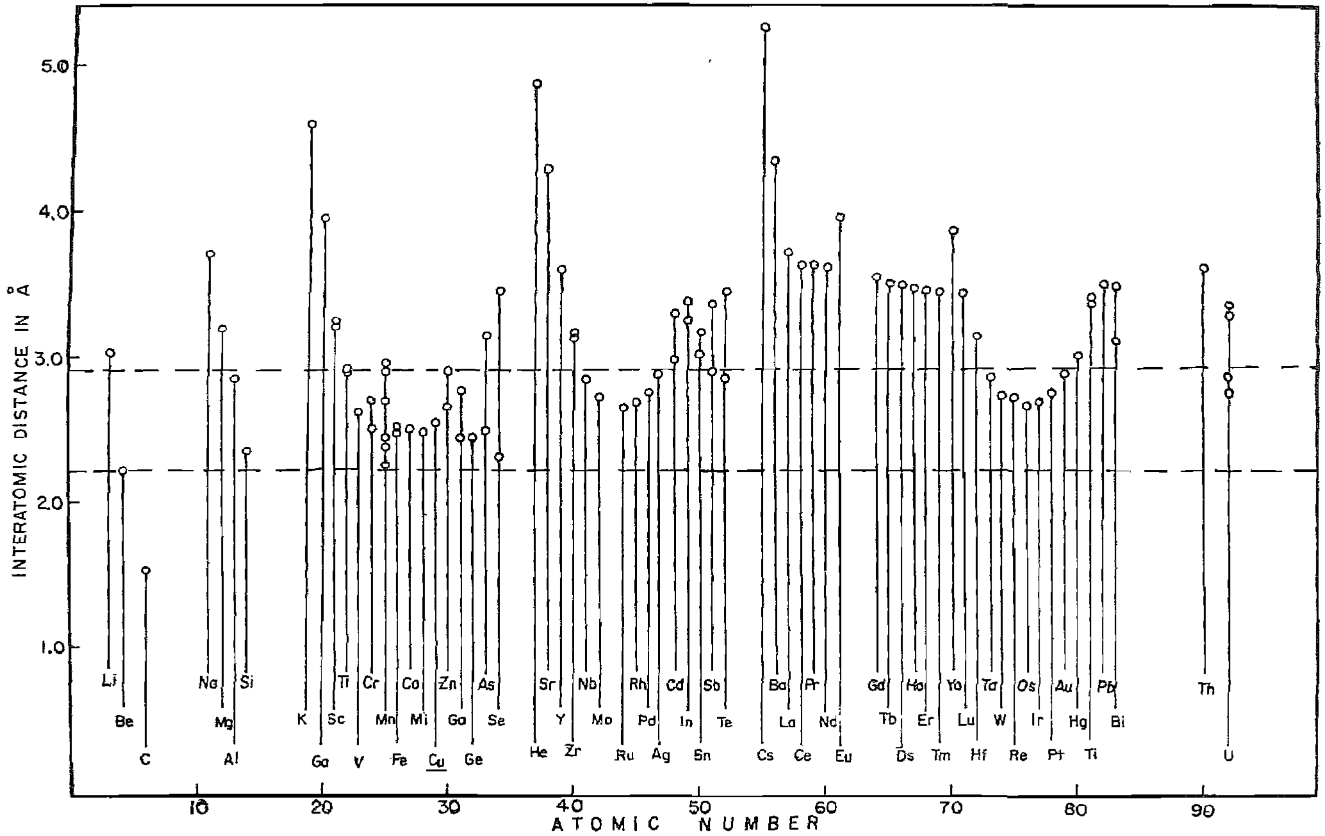

FIGURE 20-4. Closest distance of approach of atoms in the crystals of the elements. Where the crystal structure is complex, or there are allotropic modifications, more than one distance is given for the element. The dotted lines are drawn at approximately 14 per cent above and below the interatomic distance for copper.

where there is some restriction of solid solution by size-factor effects, that solid solubility decreases markedly with decreasing temperature, one of the necessary features of an age-hardening alloy. For example, beryllium is just within the favorable zone for copper (12 per cent), shows a marked fall of solubility with temperature when in solid solution in copper, and such alloys show marked age-hardening.

Electrochemical Factor. Even when the size factor is favorable, a tendency to form stable compounds will tend to limit the extent of solid solution[25]. In a general way, the more electronegative, relative to copper, is the solute element, the greater will be the tendency to form stable intermediate phases, of ionic or homopolar nature.

The reason for the limitation of solid solution is easily seen from a consideration of free-energy curves, as in the hypothetical diagrams of Figure 20-5. The thermodynamically stable structure for an alloy is that structure which possesses the lowest free energy; where a two-phase structure is stable its free energy is given by a point on the tangent between the free-energy curves of the constituent phases. In Figure 20-5, *A* is the free-energy curve for the solid solution, *B* and *C* free-energy curves for two intermediate phases, *C* being very stable, *i.e.*, with a large negative free energy. The limit of the two-phase field at the lower solute concentration, and hence the maximum solid solubility, *S*, is much less for the systems containing the highly stable compound *C* despite identical free-energy curves for the solid solutions.

Copper is not strongly electropositive, and the only elements of favorable size factor which are strongly electronegative are those of Group VIB,—sulfur, selenium, and tellurium. Here the tendency to form stable compounds does, in fact, very much restrict solid solution. The elements of Group VB are less electronegative, and might form an intermediate case. Only arsenic, however, has a favorable size factor. Here the maximum solid solubility, 6.9 atomic per cent arsenic[29], is, in fact, less than the maximum possible solubility.

Relative Valency Effect. The tendency for two metals to form solid solutions in each other is not necessarily reciprocal, and a "relative valency effect" has been proposed[30]. This states that, other things being equal, a metal of lower valency is more likely to dissolve one of higher valency than vice versa. This rule is not universally obeyed, and can be considered to be a combination of several separate factors, each of which tends to limit the solubility of an element of lower valency in one of higher valency. In the formation of alloys copper is usually considered to be monovalent, so that the solid solubility of copper in other elements of favorable size factor is limited by the operation of this relative valency effect.

Other Valency Effects. Consideration of cases where the size factor and electrochemical factor favor extensive solid solution leads to a further valency effect which eventually limits solid solution.

Hume-Rothery has shown that, in general, many features of phase

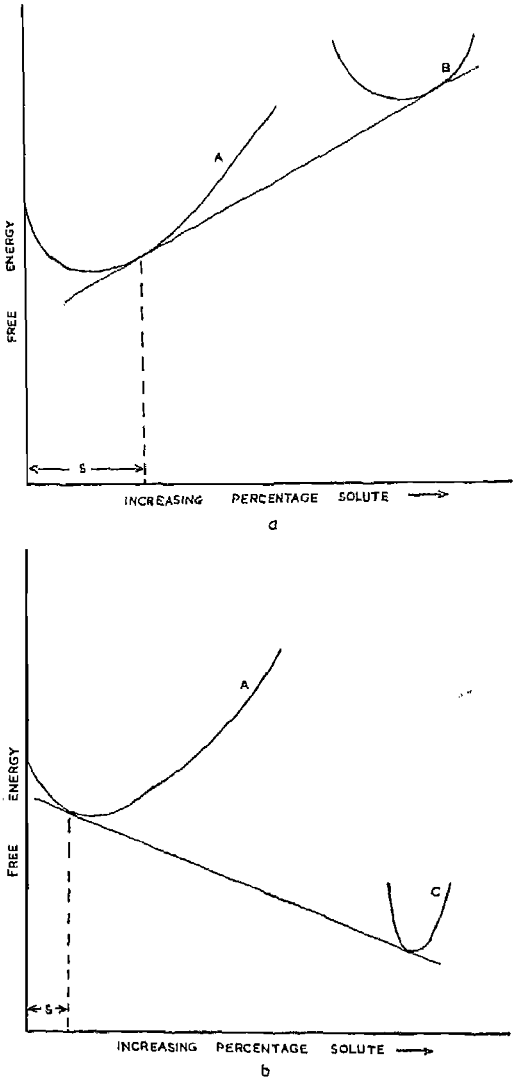
FREE ENERGY
B
A
S
INCREASING PERCENTAGE SOLUTE →
a
FREE ENERGY
A
C
S
INCREASING PERCENTAGE SOLUTE →
b

FIGURE 20-5. Hypothetical free-energy curves showing equilibrium between a solid solution and (*a*) a normal intermetallic phase, and (*b*) a highly stable intermetallic phase. Although the free-energy curve of the solid solution is the same in both, the maximum solid solubility *S* is greater in (*a*).

diagrams are associated with a definite ratio of the number of valency electrons to the number of atoms in an alloy. In particular he showed that in a large number of alloy systems based on copper, silver, or gold, where the size factor was favorable, that the maximum solid solubility corresponded to an electron:atom ratio of approximately 1.4. Thus the divalent element zinc dissolves in copper up to a limit of approximately 40 atomic per cent (actually 38.4 atomic per cent Zn), the trivalent element aluminum to a limit of approximately 20 atomic per cent (actually 20.4 atomic per cent Al), and the tetravalent element germanium to approximately 13.3 atomic per cent (actually 12.0 atomic per cent Ge).

Hume-Rothery's empirical observation has received support from quantum theory[32, 33]; however, only a brief outline can be given here. An electron can be considered to be a wave system of wave length $\lambda = \frac{h}{mv}$, where h is Planck's constant, mv the momentum of the electron. The kinetic energy of a free electron is $E = \frac{mv^2}{2} = \frac{h^2}{2m\lambda^2}$, or $\frac{h^2k^2}{2m}$, where k is the wave number, equal to $\frac{1}{\lambda}$. In the "free electron" quantum theories, the valency electrons of the solid metal are considered to occupy a series of quantum states of increasing energy (and hence increasing k). Each state, by Pauli's exclusion principle, can contain a maximum of two electrons of opposite spin. However, at some critical wave number (k_c) and wave length (λ_c) for an electron moving in a specific direction in the metal crystal, the wave length may satisfy the Bragg relationship $\lambda = 2d\sin\theta$, for reflection from a certain set of atomic planes of spacing d at an angle θ to the direction of motion of the electrons. "Reflection" implies that the electrons would be rejected from the crystal if moving with this wave length in this direction; *i.e.*, this is a "forbidden" motion. As a result there is a forbidden wave number (k_c) and a forbidden range of energy. The resultant curve of energy versus k is shown in Figure 20-6. $\triangle E$ is the forbidden range of energies. The critical value of k will depend on the direction of motion of the electron in the lattice, being different for different directions in the lattice. Three-dimensional figures can be drawn showing k_c for all possible directions in the crystal lattice of the metal. These figures, drawn in "k-space," are known as Brillouin zones. These figures are polyhedra, each face of which corresponds to a particular set of lattice planes. As in the one-dimensional case of Figure 20-6, there is a discontinuous jump in energy between k values just below and just above k_c; *i.e.*, just inside and just outside a Brillouin zone.

The first Brillouin zones for the face-centered cubic and body-centered

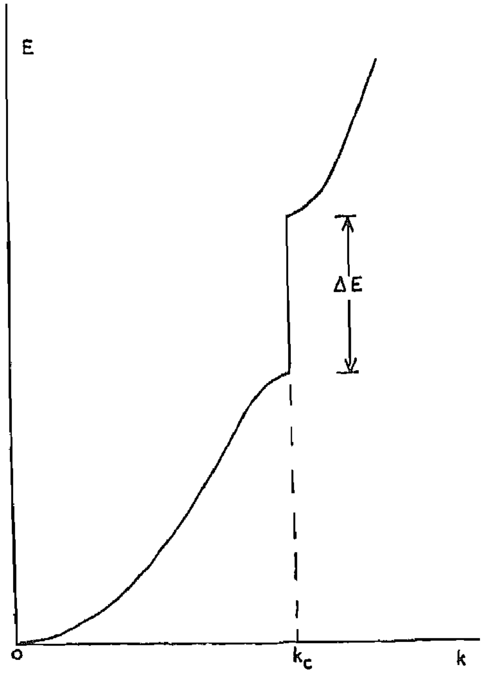

FIGURE 20-6. Relationship between electron energy E and wave number k for an electron moving in a periodic field such as a crystal lattice.

cubic lattices, that is, the zones closest to the origin of k-space, are shown in Figure 20-7. For any specific direction the electron energy and wave number are related in the manner of Figure 20-6, and contours of constant electron energy can be drawn in k-space. Near the origin these contours are spherical surfaces, but as the zone faces are approached the contours are distorted through the anomalous curvatures near k_c shown in Figure 20-6. Each of these zones can be considered to contain two electrons per atom.

An alternative method of plotting is the "$N(E)$ curve." This ignores the dependence of electron energy on direction in the lattice, summing the effects of all directions in one curve. It is a plot of the number of energy states per unit volume between the energies E and $(E + dE)$ against E. This has the form of Figure 20-8. The total energy of the electrons is given by the area under the curve up to the state of greatest E that is occupied.

With this introduction we may return to Jones' explanation of Hume-Rothery's observation. He noted that, in very many copper, silver, and gold-based alloys, the second phase had a body-centered cubic structure.

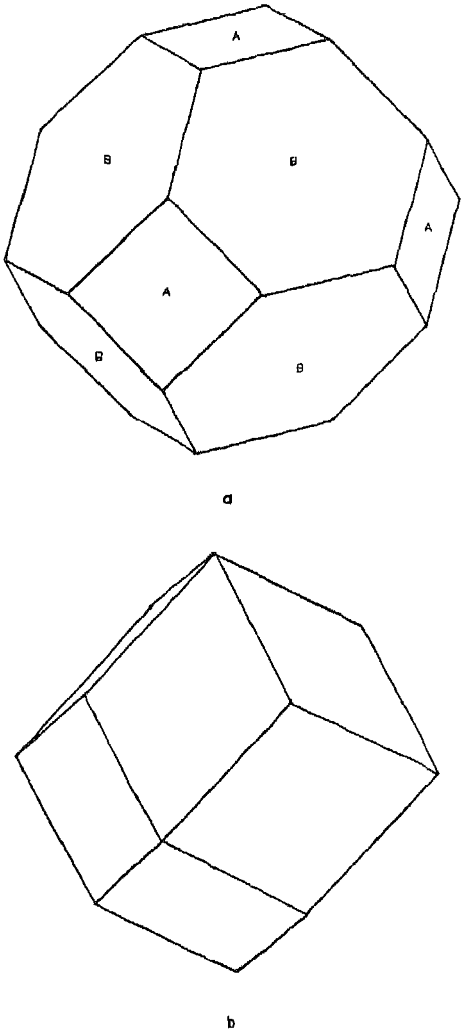

FIGURE 20-7. First Brillouin zones for (*a*) face-centered cubic lattice and (*b*) body-centered cubic lattice. The faces *A* and *B* in (*a*) are derived from the {200} and {111} lattice planes, respectively. The faces in (*b*) are derived from {110} lattice planes.

The $N(E)$ curves for the body- and face-centered cubic lattices are both plotted in Figure 20-9(a). The peak of the curve is reached first for the face-centered cubic lattice. The difference in total electron energy for varying electron:atom ratio has been derived from these two curves and is given in Figure 20-9(b). The difference is negative for electron:atom ratios below about 1.4, positive beyond this value. Thus, if the only

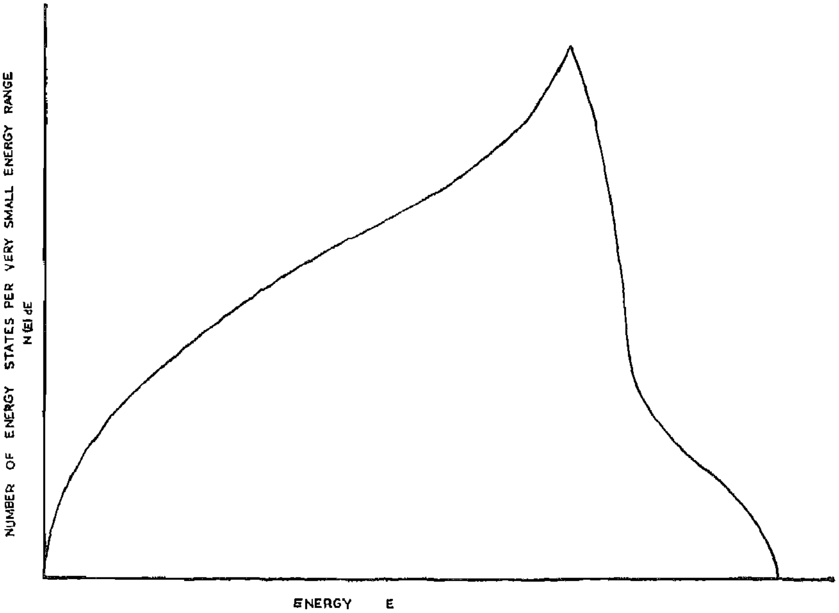

FIGURE 20-8. $N(E)$ curve.

factor determining the energy of the structure as a whole is the electron energy, the face-centered cubic lattice would be the stable structure for electron:atom ratios up to 1.4, and the body-centered cubic lattice stable at higher electron concentrations. By certain simplifying assumptions about specific heat, Jones was able to calculate the $\alpha/(\alpha+\beta)$ and $(\alpha+\beta)/\beta$ boundaries, and their change with temperature. His results, as can be seen from Figure 20-10, were in good agreement for the systems copper-aluminum and copper-zinc.

Brillouin zone theory, has, of course, a wider application. As a general rule it can be stated that the electron energy is lowest in a structure in which the Brillouin zone is nearly full; *i. e.*, when the maximum electron energy corresponds to a point on the $N(E)$ curve just beyond the peak. Where the electron energy is an important factor in the stability of a phase, this implies that a crystal structure may be adopted for which the Brillouin zone is nearly full, and provides an elegant interpretation of the structures of "electron compounds."

This treatment ignores all effects except those due to electron energy; in fact, size and other factors have an influence. Where the size factor is unfavorable or borderline the maximum solid solubility will be less than that given by theory. In a more detailed study of the effects of size factor on solid solubility in copper, Hume-Rothery[31] showed that where

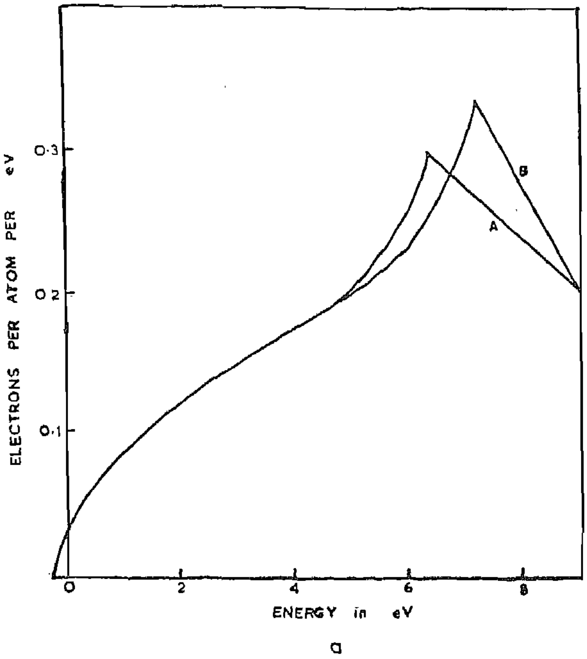

Figure 20-9a. $N(E)$ curves for (a), face-centered cubic lattice; (b), body-centered cubic lattice.

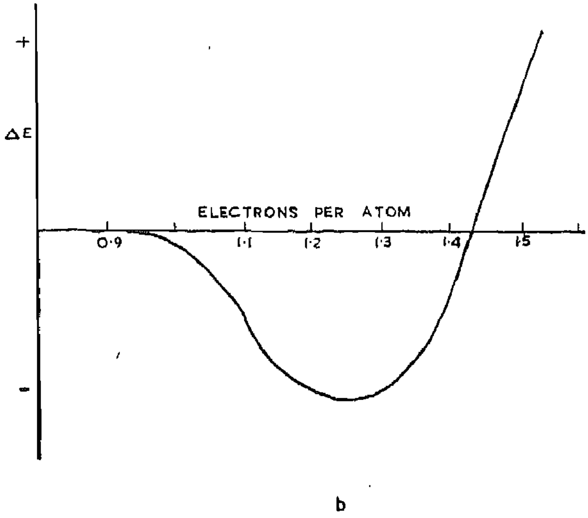

Figure 20-9b. Difference in electron energy, at various electron:atom ratios, of the face-centered cubic and body-centered cubic lattices.

the mean distortion of the lattice at the solubility limit was less than 0.07 to 0.09Å, the electron:atom ratio was affected only slightly (copper-zinc, copper-gallium, and copper-aluminum). With larger distortions, due to elements near the borderline of favorable size, there is a marked fall in the electron:atom ratio at the solubility limit (copper-tin and copper-indium). Where the size factor is definitely unfavorable the mean lattice distortion never reaches the limit of 0.07 to 0.09Å, presumably due to the intense local distortion around each solute atom.

This explanation is not entirely satisfactory, and to some extent this may be due to the inadequacy of the concept of size factor. For example, the solubilities of cadmium, indium, tin, and antimony in copper are restricted by unfavorable size factors. However, as we pass along this

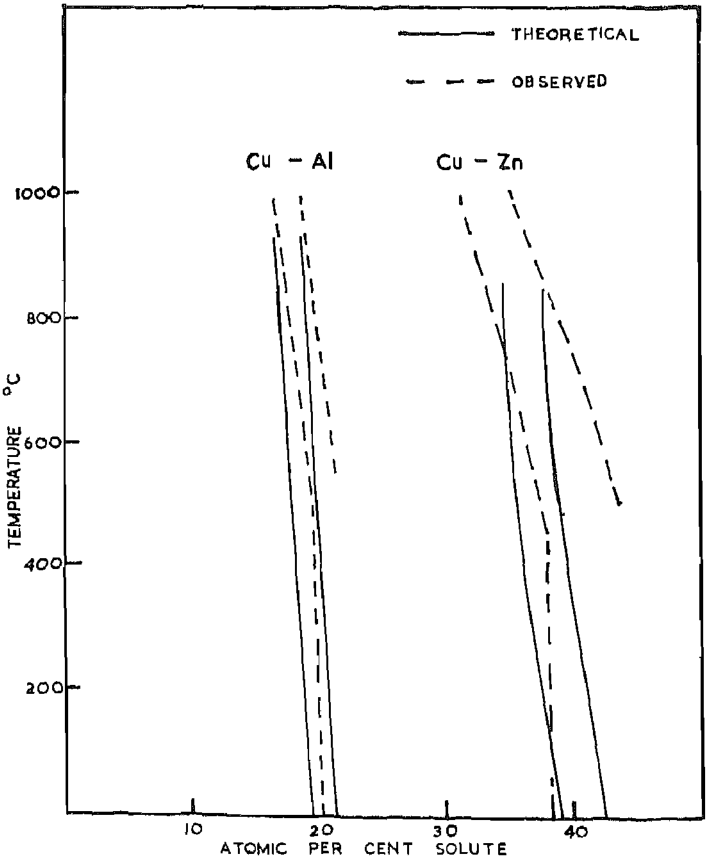

FIGURE 20-10. Calculated and observed phase boundaries in the copper-zinc and copper-aluminum systems.

series, the solubility in terms of electron:atom ratio approaches progressively the theoretical value of 1.4 electrons per atom, as shown in Table 20-2.

TABLE 20-2. MAXIMUM SOLID SOLUBILITIES IN SOME COPPER-BASE SYSTEMS

System	Solid solubility, atomic per cent	Electrons per atom
Cu-Cd	1.7 Cd	1.02
Cu-In	10.9 In	1.22
Cu-Sn	9.26 Sn	1.27
Cu-Sb	5.9 Sb	1.24

This has been attributed to the ionic size, that is, the size of the metal ion in a crystal of a salt-like compound. The ionic diameters decrease progressively on passing from cadmium to antimony, and it is suggested[34] that as a result it becomes easier to insert the solute ions in the copper lattice. Thus ionic sizes may have a secondary influence as a type of size factor.

From the above discussion it can be seen that complete solid solution throughout a binary system is only possible where size factors are favorable, the electrochemical factor is small, the valencies of both elements are the same, and where both elements have the same crystal structure. For copper these considerations are only fulfilled by silver and gold, and even here the size factors are near the border of favorable size (12.5 per cent in each case). In fact the system copper-gold shows complete solid solubility, the system copper-silver shows limited solutions. This difference of behavior despite an identical size factor has been attributed to the fact that the gold ion is more easily polarized than the silver atom, and can thus be more easily fitted into the copper lattice. These, and other modifications of the size-factor concept, are discussed by Hume-Rothery and Raynor[34, 35].

Lattice Parameters. Valency effects have also been demonstrated in the lattice parameters of solid solutions in copper. In dilute solid solutions a plot of lattice spacing against composition is almost linear. Owen[36] has used the slopes of such curves, as distortion per atomic per cent solute; and when plotted against valency certain regularities are shown. Figure 20-11 gives this type of plot for elements of the B subgroups of the first and second long periods in solid solution in copper. The reasons for the deviations of cadmium, silver, and arsenic are obscure.

Further regularities are shown in the relationship between total lattice distortion at maximum solubility (*i.e.*, $\frac{\delta a}{a}$, where a is the lattice spacing) and the total volume of solute element entering the lattice at maximum solubility[36] (Figure 20-12). Arsenic, again, shows anomalous behavior. The straight lines extrapolate to the origin of the plot, and fit the expression

$$\frac{\delta a}{a} = bvS_m$$

where S_m is the maximum solubility in atomic per cent, v is the atomic volume of the solute, and b is a constant having a different value for each of the two series. Similar observations have also been made for gold and silver-based alloys.

Valency thus plays a considerable part in determining lattice spacing; we can note that in some systems a lattice expansion is produced by a

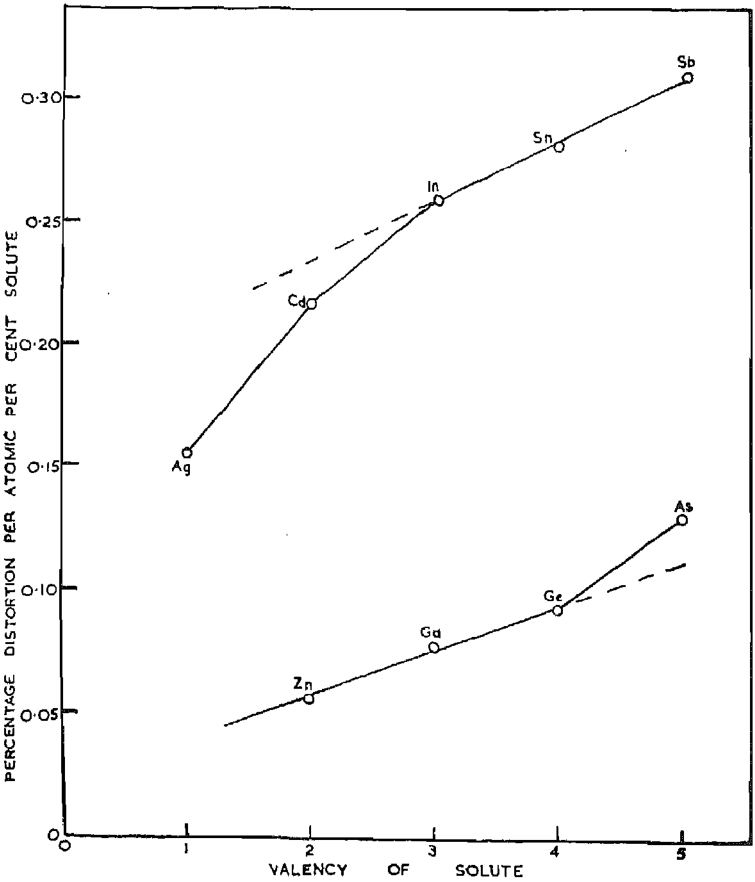

Figure 20-11. Lattice distortion in solid solutions in copper[36].

solute element whose atomic diameter is less than that of copper, for example, germanium.

Transitional Metal Solutes. Most of the systematic study of solid solutions in copper has been concerned with metals of the B subgroups of the periodic table. Study of other solutes has been less extensive; in particular, the effects of transitional elements as solutes have not been fully explained. Study of intermediate phases formed by transitional elements suggests that both valency and size factor may vary with the structure in which the transitional element is present. It does appear that, in general, the size-factor rule is applicable to transitional metal alloys, and this must in part explain the complete series of solid solutions which nickel, platinum, palladium, etc., form with copper. Recent work on ternary copper-base alloys[60] suggests that the transitional elements manganese, iron, cobalt, and nickel, when present in dilute solid solution in copper, exert valencies of 1.83, 1.0, 0.8, and 0.6, respectively. These valencies will not necessarily apply, however, when the transitional elements are present in greater concentration. This work has been discussed theoretically by Jones[61].

In all the above discussion it has been assumed that copper is monovalent in metallic structures; *i.e.*, that only the 4*s* electron is effectively

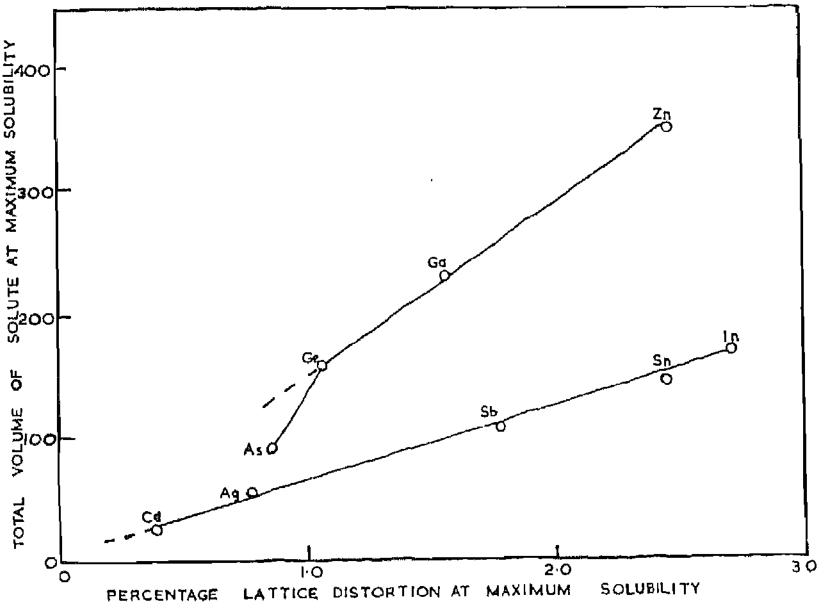

FIGURE 20-12. Lattice distortions at maximum solid solubility for solid solutions in copper[30].

free. A differing point of view is held by Pauling[37, 38, 39], whose resonating valence bond theory assigns a valency of 5.5 to copper. This theory has had considerable success in the interpretation of interatomic distances, and cohesion, and can be reconciled with Brillouin zone considerations for many intermetallic compounds[38, 40]. Pauling's theories have been critically reviewed by Hume-Rothery[41]. It is difficult at present to see how the two differing viewpoints on the behavior of copper can be reconciled.

Solidus and Liquidus Lines

Though less extensively studied, primary solidus and liquidus curves show size factor and valency effects. The effect of valency was demonstrated by Hume-Rothery and Reynolds[42]; liquidus curves of silver alloys were determined accurately, and could be made to coincide to a high degree of accuracy when plotted to a base of equivalent composition, *i.e.,* atomic per cent of solute multiplied by its valency. Figure 20-13 shows the liquidus curves of the binary systems of copper with zinc, gallium, germanium, or arsenic plotted in an analogous manner; Figure 20-13(a) shows the liquidus curves to a base of atomic percentage, Figure 20-13(b) to a base of electron:atom ratio. The points are taken from published diagrams, and the coincidence is seen to be good. These elements are in the same period as copper, and all have favorable size factors. In other cases the agreement is not always so good; however, in many systems where the size factor is favorable the same rule seems to apply. Thus the liquidus curves of the tetravalent elements silicon and germanium in copper are almost coincident when plotted in atomic per cent. Hume-Rothery has also shown that this rule can be extended to cover ternary and higher systems of such favorable elements, so that it is possible to calculate liquidus temperatures of ternary alloys to a good degree of approximation.

A theoretical explanation of this rule has been advanced by Jones[43].

Similar valency effects have been noted in solidus lines. Hume-Rothery[25, 28] considered the elements of Groups IIB, IIIB, and IVB as solutes in copper, and showed that where size factors were favorable the depression of the solidus curves (in degrees C per atomic per cent solute) was roughly proportional to the square of the valency of the solute. The effect of size factor is more marked for solidus than for liquidus curves. Aluminum in copper seems to be an exception to these rules; the slopes of both liquidus and solidus are abnormally small.

INTERMEDIATE PHASES IN COPPER SYSTEMS

Intermediate phases in metallic systems can be of varied types and it is possible to trace a transition from phases in which the intermetallic

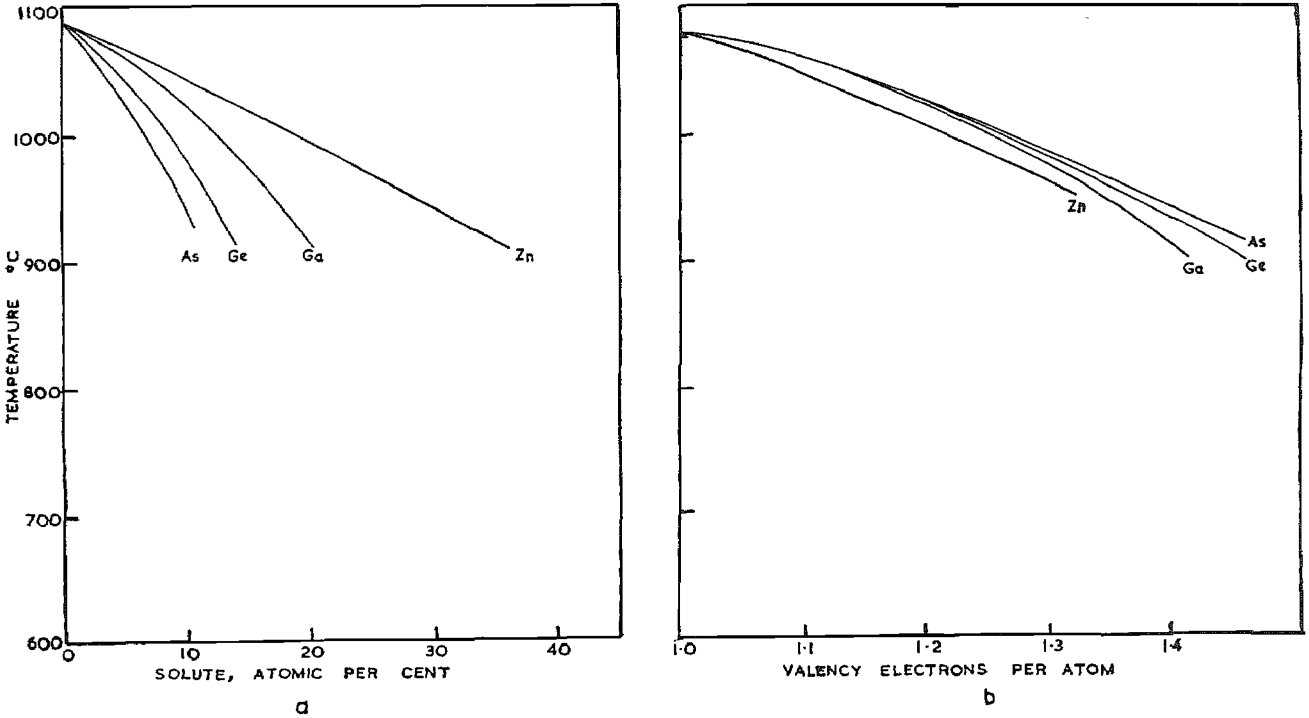

FIGURE 20-13. Liquidus curves of various copper-base systems plotted to a base of (*a*) atomic per cent and (*b*) electron:atom ratio.

linkage is purely metallic to phases in which the linkage appears to be purely homopolar, or ionic. In some phases the component elements show their normal chemical valency, but in very many intermediate phases, as can be expected where the binding is metallic, the normal chemical valency rules do not apply. This type of compound frequently exists over a range of composition, again unlike normal valency compounds. The first group of compounds to be dealt with are of this latter type.

Electron Compounds

The body-centered cubic β phases which occur in many copper systems next to the primary solid solution in copper have already been mentioned. They are one type of "electron compound," in which the crystal structure and composition are controlled mainly by the establishment of a certain electron:atom ratio.

3/2 Electron Compounds. These, the β phases, are characterized by a ratio of three valency electrons to two atoms; their crystal structure is in general body-centered cubic, either ordered or disordered. They may occasionally have close-packed hexagonal or β-manganese structures. The first Brillouin zone for the body-centered cubic structure (Figure 20-7, b) contains 2 electrons per atom when full; the Fermi surface first touches the faces of the zone at 1.48 electrons per atom. The characteristic ratio of 1.5 electrons per atom lies between these two values, and is just beyond the peak of the $N(E)$ curve. It is thus in agreement with the rule given earlier.

Typical examples are CuZn, Cu_3Al, Cu_5Sn (body-centered cubic), Cu_3Ga (close-packed hexagonal). Most 3/2 electron compounds show a range of homogeneity; some, like Cu_3Al, are only stable at high temperatures, and decompose eutectoidally at low temperatures to another phase plus the primary solid solution. In other systems two of the possible structures may occur at different temperatures; thus in the copper-gallium system there is a high-temperature β phase which is body-centered cubic, and a low temperature β phase which is close-packed hexagonal.

Although the electron:atom ratio is the overriding factor in the occurrence of these compounds, the details of composition, homogeneity range, and crystal structure are sensitive to other factors, including size factor, temperature, and solute valency, as Hume-Rothery, Reynolds, and Raynor[44] have shown. They demonstrated the following general trends:

(a) Increasing solute valency favors the β-manganese or close-packed hexagonal structures at the expense of the body-centered cubic structure.

(b) Increasing temperature favors the body-centered cubic structure at the expense of other types.

(c) Increasing size factor favors the body-centered cubic phases at the expense of the other types, and tends to displace the homogeneity range to lower electron:atom ratios, and to restrict the homogeneity range in terms of both electron:atom ratio and temperature.

(d) Copper is less likely to form ordered body-centered cubic phases than silver or gold. This is ascribed to the greater electrochemical factor for these latter metals.

21/13 Electron Compounds. The next phase to the β phase in the copper-zinc system is the γ phase, Cu_5Zn_8, with a complex crystal structure with 52 atoms in the unit cell. There are entirely analogous compounds in other systems and they can also be considered to form a group of electron compounds with the characteristic electron:atom ratio of 21 valency electrons to 13 atoms. Typical phases of this group are Cu_5Zn_8, $Cu_{31}Sn_8$, Cu_9Al_4. The homogeneity range is, in general, less than for the 3/2 electron compounds. Size-factor effects can be noted; although Cu_5Cd_8 and Cu_5Zn_8 have the same structure, the actual arrangement of atoms in the various atomic sites differs due to the difference in size of the cadmium and zinc atoms[45].

It is of interest to note that the γ-brass structure, although complex, can be derived from a body-centered cubic arrangement by stacking together 27 unit cubes to form a large cube with 54 atoms, and then omitting two atoms to give 52 atoms to the unit cell. It has been suggested[46] that this is an example of a general tendency in copper, silver, and gold alloys to form structures derived from the body-centered cube wherever possible. There are also analogies between the γ-brass structure and another structure commonly found among intermetallic phases, the nickel-arsenide structure.

The first Brillouin zone for this structure has been calculated by Jones[47]. Complete filling of the zone corresponds to an electron:atom ratio of 1.73; the inscribed Fermi surface first touches the zone faces at 1.54 electrons per atom. The characteristic ratio 21/13, *i.e.* 1.615, lies between these values and agrees with the general rule given earlier.

Other factors influence the details of the occurrence of these phases, including the following[48]:

(a) Increasing size factor displaces the composition to lower electron: atom ratios.

(b) The homogeneity range is widest when the size factor is moderate, and is less for very favorable, and rather unfavorable, size factors. Where the size factor exceeds 20 per cent no γ phases are formed.

(c) Increasing electrochemical factor displaces the composition to higher electron:atom ratios. It is suggested that this is due to the stabilizing effect of higher electrochemical factor on the neighboring β phases.

(d) Careful work on Cu_9Al_4[49] and Cu_9Ga_4[50] has shown that defect lattices, in which atoms are omitted from certain lattice points, are formed at higher solute content in such a way that the number of electrons per unit cell tends to remain constant. Since it is the lattice structure that determines the Brillouin zone, it is essentially the number of electrons per unit cell, rather than electrons per atom, that determines the total electron energy. The formation of such defect lattices is thus a striking confirmation of the important role of electron energy in determining these structures.

These workers[48] also discuss the use of the Pauling valencies, and conclude that they lead to less satisfactory generalizations than the use of normal valencies.

7/4 Electron Compounds. This group of electron compounds is characterized by a ratio of 7 valence electrons to 4 atoms, and a close-packed hexagonal structure. The close-packed hexagonal structure is, of course, a common one which could arise from other effects than those of valency. Typical phases are $CuZn_3$, Cu_3Ga, and Cu_3Ge.

In general, electron compounds of these three types will only be formed in copper alloys when the size factor is less than 20 per cent, and where the electrochemical difference is not strong. Outside these limits other types of intermediate phases may be formed.

Nickel Arsenide Phases

These phases have the formula *AB*, with metalloid atoms on a close-packed hexagonal lattice, and metal atoms in the octahedral holes of this lattice. Fairly wide ranges of homogeneity may occur; and certain compounds, such as Cu_2In, with compositions well away from the equiatomic ratio, have the same basic structure. The two copper-base examples are CuSn and Cu_2In. It has been considered to be an electron compound with the ratio of 5 electrons to 2 atoms, and a determination of the Brillouin zone[51] supports this view. In the case of Cu_2In, though there are not 5 electrons to 2 atoms there are 10 electrons per unit cell of 2 molecules, and this agrees with the Brillouin zone interpretation.

Fluorspar Structure

A number of copper-bearing phases are anti-isomorphous with the fluorspar (CaF_2) structure, with copper atoms in the positions occupied by fluorine atoms in fluorspar. These phases have little homogeneity range, show many analogies to ionic crystals, and they can be considered to be normal valency compounds. Mott and Jones[63], however, show that the first Brillouin zone of this structure can contain just 8 electrons per 3 atoms, and consider that these are essentially electron compounds with the Brillouin zone completely filled. These compounds are usually formed between elements of very different electrochemical nature, and they are perhaps best considered as a transition structure between the ionic and metallic types of compound. Phases with this structure include Cu_2S, Cu_2Se, and the ternary phases CuMgSb, CuBiMg, and CuCdSb, all with 8/3 electrons per atom.

Laves Phases

These have the formula AB_2, and include three related structures, typified by the compounds $MgCu_2$, $MgZn_2$, and $MgNi_2$. Their essential feature is the satisfaction of certain geometrical considerations; a very close packing of atoms is obtained with these structures when $D_A/D_B = (1.5)^{\frac{1}{2}} = 1.225$, where D_A and D_B are the diameters of the A and B atoms. Observed ratios lie between 1.2 and 1.3. The close packing is reflected in the high coordination numbers; each A atom has 12 B neighbors and 4 A neighbors, a coordination number of 16; each B atom has 12 neighbors. Such a high coordination number implies metallic bonding, but the essential feature of the existence of these phases is the close packing made possible by the favorable diameter ratio. Other factors can influence which of the three types of structure is adopted, and this has been elucidated by work on ternary systems.

The major copper-base example is $MgCu_2$. When copper is partly replaced by zinc in $MgCu_2$, this structure persists up to 1.8 electrons per atom and is succeeded by the $MgNi_2$ and $MgZn_2$ structures. When copper is replaced by aluminum in this phase the $MgCu_2$ structure persists to 1.8 electrons per atom, is succeeded by the $MgNi_2$ structure to 2.07 electrons per atom at high temperatures and 1.88 electrons per atom at low temperatures, and finally the $MgZn_2$ structure occurs up to the maximum electron:atom ratio of 2.15[52, 53]. The general conclusion is that the $MgCu_2$ structure is characterized by a low electron:atom ratio, the $MgZn_2$ structure by an electron:atom ratio of about 2, and the $MgNi_2$ phase may appear at a somewhat indeterminate value between these two phases. A recent survey[54] confirms these effects, and shows that the exact diameter ratio also plays a part in determining the structure adopted.

$CuAl_2$

$CuAl_2$ is a representative of a further group of phases of the formula AB_2 which appear to be determined by considerations of size factor, such that D_B/D_A is approximately 1.2.

Summarizing, we may say that electron compounds of the β, γ, and ϵ brass types will only form where the electron:atom ratio is between 1 and 2, the ratio of atomic diameters is less than 1.2, and the electrochemical factor is fairly small. With suitable diameter ratios the $CuAl_2$ or Laves phase structures may appear. When the electrochemical factor is higher, nickel arsenide phases may appear, and eventually fluorspar structures. Finally, when the diameter ratio exceeds about 1.38 no intermediate phases will occur. There are still many copper-bearing phases which have not yet been classified, in particular many phases of copper with transitional elements.

TERNARY EQUILIBRIUM

The study of ternary equilibrium has proved very useful in the elucidation of alloying behavior, and some examples have already been given.

Hume-Rothery[55] has shown that in a ternary system ABC, with a compound of substantially fixed composition B_xC_y, the solid solubility isothermals and liquidus isothermals of B and C in A may follow a type of solubility-product law:

$$[B]\mathrm{x} \times [C]\mathrm{y} = \text{constant } K$$

Square brackets refer to atomic percentages corresponding to points on an isothermal; *i.e.*, a (liquid)/(liquid $+ B_xC_y$) isothermal or $\alpha/(\alpha + B_xC_y)$ isothermal. K varies with temperature; a relationship of the form $d(\log K)/dT = -Q/RT^2$ is found where T is the absolute temperature and Q is a constant related to the heat of formation of the compound. Rigorous expression of these formulas should include volume concentration and activity coefficients, but these simple expressions give reasonable accuracy.

These rules have been shown to apply in the systems copper-magnesium-silicon (compound Mg_2Si) and copper-nickel-tin (compound Ni_3Sn_2).

In ternary copper alloys the solid solubility isothermals are controlled mainly by electronic and size effects. Where size factors are favorable, as in copper-aluminum-zinc, the isothermals are straight lines joining the limits of the binary systems (Figure 20-14a). Where size factors are not favorable, the electron:atom ratio for maximum solubility tends to be depressed. Where the distortion due to one solute tends to accentuate the distortion produced by the other, there will be a deviation from the straight line as in Figure 20-14(b). This is the case in copper-aluminum-tin, copper-tin-zinc, copper-cadmium-zinc, and copper-germanium-zinc[56] alloys. In all these cases the solute elements expand the copper lattice. Where the one solute expands and the other contracts the copper lattice, relief of distortion can occur, and the solid solubility isotherms of the form of Figure 20-14(c) are found (*e.g.*, zinc-rich copper-aluminum-zinc alloys).

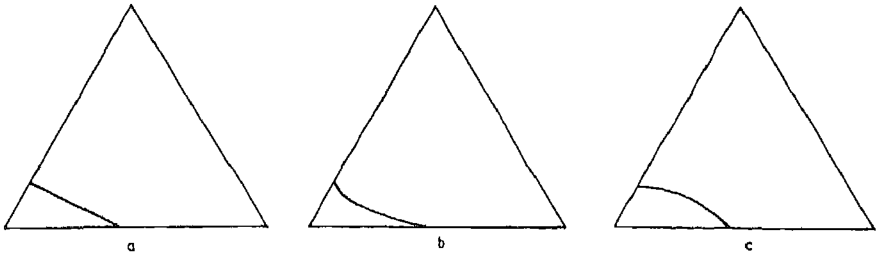

FIGURE 20-14. Possible forms of solid-solubility isothermals in a ternary system.

Many intermediate phases of the same type show complete solid solubility in each other, while maintaining the appropriate electron:atom ratio, *e.g.*, the body-centered cubic β phases in copper-tin-zinc, copper-aluminum-zinc, and copper-aluminum-tin. Similar effects are found among the γ and ϵ-brass structures; *e.g.*, there is complete solid solution between the γ phases in copper-silver-zinc, and between the ϵ phases in this system. It is possible to trace the effects of size factor, electronic effects, etc., in such ranges of solid solution[46, 57]; indeed, the study of suitable ternary systems provides a sensitive means of tracing these effects.

ORDER-DISORDER

Complete series of solid solutions, as in copper-gold, copper-platinum, and copper-palladium, usually show a random arrangement of atoms at high temperatures, but on slow cooling the atoms become rearranged to an ordered structure in which the different types of atom take up regular positions in the lattice. A perfect regular arrangement can only occur at definite simple atomic ratios, usually 3:1 and 1:1. Such ordered arrangements, or "superlattices", are found at the compositions Cu_3Pd, Cu_3Pt, Cu_3Au, CuAu, and CuPt. Ordering can occur at compositions away from ideal, but at the ideal value the ordered arrangement persists to higher temperatures, and other properties of the ordered state show maxima or minima. Ordering can also take place in intermediate phases, as in many of the 3/2 electron compounds; CuZn, for example, orders below about 460°C.

In ordered CuAu the copper and gold atoms segregate on alternate (100) planes, and the structure becomes slightly tetragonal. In Cu_3Au, Cu_3Pd, and Cu_3Pt the copper atoms occupy the face centers, and the other atoms occupy the corner sites, when ordered.

By virtue of its order, the ordered state is of lower entropy, and there must be a corresponding lowering of the internal energy of the ordered state so that it may be thermodynamically stable. Hume-Rothery and

Powell[58] point out that the alloying of two elements of different atomic size must lead to lattice strains, which will be largely reduced by ordering, so lowering the internal energy. Evidence for this includes:

(a) AuCu becomes slightly tetragonal on ordering; *i.e.*, the random strain of the disordered state is resolved on ordering into a change of lattice dimensions.

(b) Superlattices are found in the system copper-gold, with a size factor of 12 per cent, but not in silver-gold, with a size factor nearly zero.

The fact that there is a superlattice at $AuCu_3$, but not at Au_3Cu, suggests that the important lattice strains are produced by some large atoms among smaller ones, and not vice versa.

Lipson[59] suggests that electronic energy may play a part. Ordering produces extra x-ray reflections, which also imply electron reflections, and hence extra Brillouin zones. Although the energy gap across such zones must be small, their occurrence might cause a lowering of electron energy. The first such superlattice zone for Cu_3Au can contain one electron per atom, and thus may have some effect, but there is little definite evidence that any such electronic effect makes a significant contribution to the lowering of the internal energy.

Hume-Rothery[25] also suggests that electrochemical difference may also be a factor; so that superlattice formation, in this view, shows a trend to the ionic type of bond. This is supported by the evidence on ordering in 3/2 electron compounds, mentioned earlier, in which ordering was more likely in β phases based on silver and gold than in copper-base alloys, due to the higher electrochemical factors with the former metals.

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Chapter 21

The Isotopes of Copper

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In 1816 the English physician W. Prout suggested that all the chemical elements might be built up from hydrogen, and thus their atomic weights would turn out to be integral multiples of the atomic weight of hydrogen. However, most elements were found not to obey this law. Thus copper, which should have had an atomic weight of 63 or 64, was found to have a weight of 63.54 on the usual atomic scale. Consequently the Prout hypothesis was abandoned. The idea that mixtures of atoms might be involved, each an integral multiple of the weight of hydrogen, does not seem to have occurred to physicists and chemists of that age.

The present view is that all atoms are built up from three primary particles—electrons, protons, and neutrons. Electrons are very light, negatively charged particles. Protons are H^1 hydrogen atoms from which the electrons have been stripped; they are about 1,835 times as heavy as electrons and carry a positive electric charge equal to that of the electron. Neutrons are uncharged particles with mass nearly the same as the proton. Protons and neutrons are bound together in certain patterns to make up the small heavy central core or *nucleus* of the atom, while electrons, varying in number up to the number of protons used for building up the nucleus, surround the latter like a cloud, again in well-known patterns.

The chemical and many of the physical properties, including especially the optical and x-ray spectra, are determined by the behavior of the electrons in the cloud surrounding the nucleus. The discussion of these is in the province of spectroscopy, so they will be mentioned only insofar as they become directly involved in the behavior of certain copper nuclei.

The total number of protons in any given element is an invariant, and determines the place in the periodic table that is occupied by that element. It is called the *atomic number* and is denoted by Z. The number of neutrons may vary within certain fairly narrow limits, and thus the mass of a given nucleus (and hence its corresponding atom) may vary. Such variants of one and the same chemical element differing only in their mass were named *isotopes* by the British physicist F. Soddy, indicating that they occupied the same place in the periodic table.

The total number of heavy particles, *i.e.*, protons plus neutrons used for a given nucleus, is called the *mass number* and is denoted by A. This number is added as a superscript to the symbol of the element when distinction between isotopes becomes desirable.

Natural copper is a mixture of two isotopes, one with 29 protons and 34 neutrons, Cu^{63}, the other with 29 protons and 36 neutrons, Cu^{65}. Exact measurement of the proportion of these has been made a number of times, and Table 21-1 gives four sets of values found by different investigators. Generally this determination is made by means of a mass spectrograph.

TABLE 21-1. ABUNDANCE OF NATURAL ISOTOPES OF COPPER

Per cent Cu^{63}	Per cent Cu^{65}	Ref.*
69.09	30.91	1
68.44	31.06	2
68.39	32.34	3
67.66	31.61	4

* Numbers indicate the reference at the end of this chapter.

If, as is usual, atomic masses are compared with that of the oxygen atom having 8 protons, 8 neutrons, and 8 electrons, and this is set at 16.0000, the electron has a mass of 0.000549 of these units, the proton 1.007581 units, and the neutron 1.00896 units. Thus the neutron is slightly heavier than the proton. When a nucleus is surrounded by a complete cloud of electrons to render it electrically neutral, *i.e.*, the number of electrons is equal to the number of protons in the nucleus, it is called an atom. Then, when we write O^{16} and specify the atomic weight as 16.0000, it is implied that the electrons are included. The hydrogen atom therefore has an atomic weight of $1.007581 + 0.000549 = 1.00813$ atomic units.

It is immediately observed that the oxygen nucleus does not have a mass equal to that of 8 times the mass of the proton plus 8 times that of the neutron. The loss of mass is accounted for by the energy that binds these 16 particles together. It is calculated according to the Einstein equation $E = mc^2$, where m is the loss of mass—the so-called *mass defect;* c is the velocity of light, 3×10^{10} cm per sec; E is the equivalent energy (ergs, if m is in grams). The mass-defect energy is radiated during the process of "fusion" of protons and neutrons—the nucleons—into an atomic nucleus.

In the case of the two naturally occurring isotopes of copper, Cu^{63} and Cu^{65}, the former has an atomic weight of 62.956, the latter 64.955 (6), each including 29 electrons. These numbers imply that Cu^{63} has a nucleus of mass 62.9402 units, and Cu^{65} a nucleus of mass 64.939 units. On the other hand, 29 free protons plus 34 free neutrons have a total mass of 63.5245 units; 29 free protons plus 36 free neutrons have a total mass of 65.5426 units. The mass defect of Cu^{63} is therefore +0.569 atomic units, and that of Cu^{65} is +0.588 units. One mass unit is equivalent to 931 million electron volts of energy (MEV), or 3.566×10^{-13} calories. Thus the binding energy of a Cu^{63} atom is 2.029×10^{-13} calories, and that of the Cu^{65} atom is 2.097×10^{-13} calories. Since there are about 6×10^{23} atoms per mole, it is not difficult to determine that the binding energy of natural copper with the abundances given in Table 21-1 is about 2×10^{9} calories per gram. This energy would be liberated in the form of radiation if natural copper were to be produced by "fusion" of the necessary protons and neutrons.

The two natural isotopes of copper are the only two stable ones, but there are known at least six others, possibly eight, with mass numbers 58, 59, 60, 61, 62, 64, 66, and 67, respectively. The existence of the first two seems doubtful, and these will not be discussed further.

The other six have a combination of protons and neutrons in their nuclei which do not permit them to attain energy equilibrium in the nucleus under the rules laid down for such states by present-day quantum theory. The nucleus is said to be *excited* to an energy level one or more steps above the lowest or *ground state.* The nuclei of these copper isotopes are all radioactive, emitting either positive particles of the mass of the electron, *positrons,* or negative electrons, *negatrons,* and together with some of these, gamma rays, *i.e.,* energetic electromagnetic radiation of the type of very short wave-length x-rays in amount determined by quantum theory as $h\nu$, where h is Planck's elementary quantum of action, $h = 6.62 \times 10^{-27}$ erg seconds, and ν is the frequency of the emitted radiation. Such a quantum is referred to as a *photon,* or *gamma photon.*

Nuclear disintegration (*decay*) by positrons is indicated by the symbol β^+. Negatron emission, also called *beta* emission or decay, is indicated by the symbol β^-. Detection of particles emitted by radioactive elements is by means of cloud chambers, ionization chambers, Geiger and scintillation counters, with or without the help of mass spectographs and magnetic fields and material absorbers for identification and separation of the different types of radiation. For a description of these, some more fundamental text such as (7) or (8) and others must be consulted.

Negatron emission or β^- decay increases the positive character of the nucleus, so that this assumes the characteristics of its successor in the periodic table. In the case of a decaying copper atom, this would be zinc with atomic number 30, composed of 30 protons and a number of neutrons equal to the difference between the parent copper's mass number and 30. Similarly, positron emission, or β^+ decay removes a positive charge from the nucleus, so that this is equivalent to reducing the positive character of the nucleus. Therefore the decayed Cu nucleus assumes the characteristics of its predecessor nickel, with atomic number 28, in the periodic table. The mass number is equal to that of the parent copper atom.

It should not be thought that in β^- decay an electron, or in β^+ decay a positron, is actually ejected from the nucleus. There is no room for an electron or a positron within the nucleus, whose radius is about 10^{-13} cm. When these particles are found to come from an atomic nucleus, they have been created outside the latter as a consequence of the emission of the equivalent amount of energy in such a manner that the energy and momentum balance required by theory is satisfied. The sign of the charge of an electron emitted by a nucleus is determined by the proton-neutron ratio of the nucleus. If more protons are required for stability, decay will proceed by β^-; if more neutrons are required, decay will proceed by β^+. Some isotopes, such as Cu^{64}, can be stabilized by either β^- or β^+ emission, and any particular nucleus can go either way. On the average, the rate or production of β^-/β^+ for a given isotope is constant for a large number of disintegrations.

The decay process is statistically characteristic for each unstable or radioactive element. It is a *random* process, yet so precisely determined in time that for each radioactive isotope *very nearly* the same fraction of a given amount disintegrates in a given time. This fraction is called the *decay constant* λ of the isotope under consideration. It is as characteristic of the element and isotope as its spectrum lines or its x-ray spectrum. It implies the exponential decay law $N = N_0 \exp(-\lambda t)$, where N_0 is the number of atoms at the beginning of the time in question, and N the number of radioactive atoms present t (seconds, minutes, hours, days, or years) later. The time $T_{\frac{1}{2}}$ required to reduce N_0 to one-half this number is called the *half life* of the isotope. It is generally used to characterize the isotope instead of λ. Thus, when 12.8-hour copper is referred to, this means the isotope Cu^{64} which has a half life of 12.8 hours.

Positrons cannot exist in the free state for any length of time. When a positron is slowed down sufficiently and meets an electron (which will nearly always be found in any given neighborhood) an *annihilation* of the entire *mass* of both positron and negatron takes place. Since the equivalent energy of an electron (or positron) is mc^2 or 512 kilo electron volts (KEV), it follows that the total energy equivalent of this process is 1.02 MEV. This energy is radiated in the form of two gamma rays, each of 0.512 MEV energy. They are emitted in opposite directions. The method of detecting these is absorption of the positron in some solid and the placing of two detectors (Geiger or scintillation counters) on opposite sides of the absorber and so connected that they will only react if simultaneous rays strike the two separate counter tubes.

Emission of a positron in general implies an excessive number of protons within the nucleus, and a mass difference between parent and product atom equivalent to at least 1.02 MEV, provided that the masses of the two atoms are equal. If the excitation of the parent nucleus is not equivalent to this, but the excess protons nevertheless present, the mechanism of K-capture takes place. The parent nucleus captures an electron from its own K-shell (or sometimes from the L-shell) of the electron cloud around the atom. Subsequently a gamma ray (photon) $h\nu$ may be emitted to take care of any additional excess energy. This decay process is called *electron-capture.* It may properly be asked how this phenomenon could be proved. When an electron from the K-shell is pulled into the nucleus to balance energy conditions there, a vacancy arises and an electron from an outer shell will be pulled into this place. The result is the emission of the characteristic x-ray from the K-shell of the daughter and is observed by Laue or Debye-Scherrer spectroscopy, or by proportional counters, scintillation counter spectrometry, etc.

The several isotopes of copper may be produced in a variety of ways by bombardment with particles in accelerators or atomic reactors. It is of interest to have some knowledge of relative efficiencies of the various processes. Cu^{64} can be produced from Cu^{63} in the atomic reactor where thermal neutrons (0.035 electron volts energy) react with the nucleus. It may also be produced by bombardment with 1 MEV neutrons. The measure of efficiency of the two processes is the *cross section,* the number of reactions obtained per projectile per target-atom in unit area. The projectile is assumed to have negligible area. The unit of cross section is the *barn,* which equals 10^{-24} sq cm and is usually denoted by the symbol σ. It is a measure of probability of the reaction taking place. Cu^{63} subjected to thermal neutrons has a cross section for Cu^{64} production of $\sigma = 2.8$ barns. The reaction is (n, γ), *i.e.*, a neutron is captured by the Cu^{63} nucleus, and a gamma emitted simultaneously. Each Cu^{63} nucleus appears

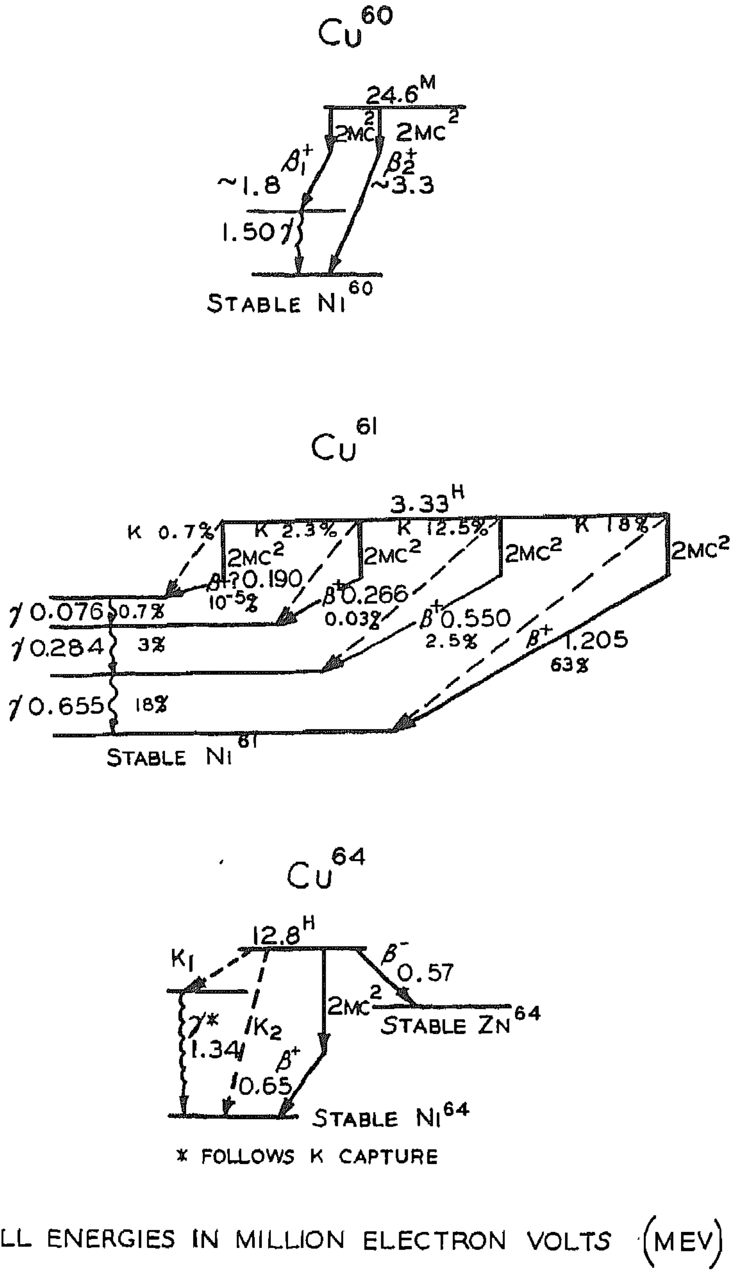

FIGURE 21-1. Decay schemes of copper isotopes. Arrows to left indicate positron emission, arrows to right negatron emission. Broken lines indicate K-capture of electrons. Beta energies are in MEV and are maximum. The difference between this and actually measured energies is accounted for by the *neutrino* hypothesis. (*From National Bureau of Standards "Nuclear Data and Supplements."*)

to the neutrons in the reactor as a target of area 2.8×10^{-24} sq cm. For the reaction $Cu^{63} + (1\ MEV\ n, \gamma) \rightarrow Cu^{64} + \gamma$, the cross section is only $\sigma = 0.009$ barns.

Table 21-2 gives a selected set of data on individual copper isotopes. Three of the radioactive ones, namely Cu^{60}, Cu^{61}, and Cu^{64} have known decay schemes, and these are shown in the diagram Figure 21-1. They are taken from the Bureau of Standards circular "Nuclear Data" (5), as are most of the properties listed in Table 21-2. For further details this very exhaustive compilation of nuclear data should be consulted. The fractions β^-/β^+, K/β^+, and γ/β^+ indicate the ratio of the rate of occurrence of particles in the numerator as compared with denominator. Production reactions are given by way of example only, and are not necessarily the ones with the largest cross section.

One gram of Cu^{64} contains about 9.4×10^{21} atoms, and its half life was already given as 12.8 hours. This implies that $(0.69 \times 9.4 \times 10^{21})/(12.8 \times 3600) = 1.4 \times 10^{17}$ disintegrations per second take place. The number 3.7×10^{10} disintegrations per second is the standard of activity used, and is called 1 curie. It follows that 1 gram of Cu^{64} is an activity of 3.8×10^{6} curies. This is equivalent to the activity of 3.8×10^{6} grams of radium.

When radioactive copper Cu^{64} is to be used for experimental purposes, such as in tracer work, the quantity obtained is measured by its activity. From the above calculation it follows that 1 microgram of this substance has an activity of 1 curie, that is, equal to that of a gram of radium. Obviously, when natural copper is irradiated in an atomic reactor, only a small fraction need be activated to represent an amount ample for experimental purposes. Activities of millicuries, and even microcuries, are quite sufficient for most purposes.

In the atomic reactor the Cu^{63} component of natural copper converts to Cu^{64} with its half life of 12.8 hours; the Cu^{65} component converts to Cu^{66} with a half life of 4.3 minutes. The latter decays into Zn^{66}, and as the ratio β^-/β^+ for Cu^{64} is about 2.0, two-thirds of the 12.8-hour isotope Cu^{64} converts to Zn^{64}; the remainder decays to Ni^{64}. As all the Cu^{66} converts to zinc, it is seen that considerable zinc contamination of an experiment may occur if large quantities of radioactive material are used.

Radioactive copper isotopes have been used in the past mainly for tracer work. For this purpose the isotope Cu^{64} seems to be the only suitable one, since the others are either too short lived, or in the case of Cu^{67} with its half life of 56 hours, production is possible only from the rare zinc isotope Zn^{67}, present in natural zinc to the extent of only 4 per cent; or from Ni^{64} by 20 MEV alpha bombardment with subsequent proton emission. Again, Ni^{64} is present in natural nickel to an amount of

TABLE 21-2. PROPERTIES OF THE ISOTOPES OF COPPER

Mass No.	60	61	62	63	64	65	66	67
Half life $T_{\frac{1}{2}}$	24.6 m	3.33 h	9.9 m	Stable	12.88 h	Stable	4.34 m	56 h
Negatron emission energy (MEV)	none	none	none	—	See decay scheme	—	2.58	0.5
Positron emission energy (MEV)	See decay scheme	See decay scheme	2.8	—	See decay scheme	—	none	none
Gamma emission (MEV)	See decay scheme. 1.5	See decay scheme	0.56	—	See decay scheme	—	1.32	?
K-capture	none	$K/\beta^+ = .38$	none	—	See decay scheme	—	none	none
Produced from, by reaction	Ni^{60} (p, n)	Ni^{61} (p, n)	Cu^{63} (p, n) Ni^{62} (p, n)	Desc. of Ni^{63}, $T_{\frac{1}{2}} = 85$ y Desc. of Zn^{63} $T_{\frac{1}{2}} = 38.3$ m	Cu^{65} (n, p)	Ni^{65} $T_{\frac{1}{2}} = 2.56$ h Zn^{65} $T_{\frac{1}{2}} = 250$ d	Cu^{65} (n, γ)	Bi fission
End product	Ni^{60}	Ni^{61}	Ni^{62}	—	Zn^{64}+ Ni^{64}+	—	Zn^{66}	Zn^{67}

only about 1 per cent. In these experiments advantage is taken of the fact that exceedingly small amounts of elements containing radioisotopes can be detected and measured. However, this advantage is somewhat offset by the fact that it is frequently very difficult to make measurements of radioactivity with an accuracy and reproducibility comparable to that expected from analytical chemistry.

Tracer work with copper has been done for determination of wear on phosphor bronzes and other copper-bearing alloys; for determination of the distribution of metal in electrodeposition of copper; and for determination of vapor pressure of the metal at different temperatures*.

Acknowledgment. Thanks are due to a number of persons who have read the manuscript and made suggestions, notably Dr. A. A. Hobbs, Jr., Radiologist, Protestant Deaconess Hospital, Evansville, Ind.

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* A report of the last-named study, by W. H. Johnston and A. W. Searcy of Purdue University, appeared in *Proc. Indiana Acad. Sci.*, 61, 114 (1951).

Chapter 22

Phase Diagrams of Copper Alloy Systems

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The phase diagrams presented in this chapter are of considerable potential aid to metallurgists concerned with melting, casting, fabrication and heat treatment of copper alloys. The usual limitations, however, must always be kept in mind: (1) that these diagrams represent equilibrium conditions which may or may not be true under industrial conditions and (2) furthermore, they represent binary or ternary systems of two or three pure components. While purity is never absolute but always relative, these systems would represent alloys relatively quite pure as compared to most commercial alloys.

The phase diagrams basically are taken from either "The Metals Handbook," 1948 edition, or from Publication No. 44 of the Copper Development Association. In a few cases, slight amendments have been made on the basis of subsequent research publications.

Not only have phase field boundaries been reproduced but also phase designations of the aforementioned diagrams have been accepted. This occasionally leads to a confusion somewhat distressing to an orderly mind. For example, even the face-centered cubic copper-base terminal solid solution does not always have the same designation. Usually it is an alpha phase, but in the copper-silver system it is called β. There are more serious confusions in terminology than this typical example and because the difficulty is universal, a movement to adopt a generalized system of phase designations is now under way. Unfortunately, the new system has not yet been accepted and could not be adopted for this collection of diagrams.

Hume-Rothery and his colleagues many years ago started a systematic investigation of phase diagrams. For the copper, silver, and gold-base systems, they evolved some brilliant generalizations[1] regarding phase diagrams of these metals with other metals in certain parts of the periodic table. With further development of the electron theory of metals, a theoretical basis was found for the earlier generalizations and this led to fruitful developments in the theory of alloys.

It now appears that to some degree, the theory based on Hume-Rothery's work and subsequent developments by Jones[2], Raynor[3], *et al.*, is a theory of the exceptions of alloys, *i.e.*, there are more alloy systems which do not follow the Hume-Rothery generalizations than those which do. However, a large number of the important copper-base systems do follow the generalizations and will be discussed briefly in terms of the theory.

When copper is alloyed with metals of the B subgroups and of the first two short periods of the periodic table, the first additions of the solute usually result in the formation of a primary substitutional solid solution. In systems where the effective size of the solute atom is within 15 per cent of the size of the copper atom and the relative size factor is therefore favorable, the limit of the copper-base alpha solid solution is reached when the electron concentration has increased to a value of about 1.36 to 1.40. This limit is never reached for univalent solutes; it is at about 36 to 40 atomic per cent for divalent solutes such as zinc, at about 18 to 20 atomic per cent for trivalent solutes such as aluminum, or at about 12 to 13 atomic per cent for tetravalent solutes such as silicon. The electron theory of metals[3], in the case of copper and also silver, has quite satisfactorily explained this limit to the face-centered cubic structure in terms of relative electronic energies of the face-centered cubic and body-centered cubic structures.

In many copper-base systems, the next stable phase upon exceeding the solute concentration for the terminal solid solution is a structure with an electron concentration of 1.5. For convenience, phases of this type are called 3/2 electron compounds. The crystal structures of these are of three types:

(1) Body-centered cubic, either disordered β or ordered β'.

(2) Close-packed hexagonal structure usually called ζ or ζ'.

(3) β-manganese structure (denoted by μ).

An examination of the data concerning these structures has led to the following generalizations[4]:

(1) Increasing valency of the solute favors the ζ or μ structures at the expense of β or β' structures.

(2) Increasing temperature favors the β structure at the expense of β', ζ, or μ structures.

(3) Increasing atomic size of the solute favors the β structures. It also moves the composition of the 3/2 electron compounds toward slightly

lower electron concentrations and narrows the composition range of the β phase.

(4) The difference in electrochemical properties of copper and the solute is also significant. Copper alloyed with an electropositive element such as magnesium is electronegative, and when alloyed with an electronegative element such as arsenic, copper is the electropositive member of the alloy. It is found that when the electrochemical difference is large, the electron compounds may no longer appear but other compounds are formed (*e.g.*, Cu_3P) and these begin to acquire the characteristics of valency compounds, *e.g.*, show long range order.

With still higher percentages of the solute element, beyond the 1.5 electron concentration, new phases are formed with a characteristic complex cubic structure of 52 atoms, the γ brass structure. Actually, this quaint structure could be considered a distorted body-centered cubic structure from which 2 atoms out of 54 have been removed. The γ phases usually include the electron concentration 1.615 and are called, for convenience, 21/13 electron compounds. Theoretical analyses of the Brillouin zone structure of the γ phase and relatedly of the many structures of this type, both in copper-base alloys, in silver- and gold-base alloys, and in alloys with transitional elements as a solvent, have led to certain generalizations regarding 21/13 compounds[5].

(1) Usually, there are a fixed number of electrons, about 87 to 88 per unit cell of the structure, and the structure becomes unstable with more than this number present.

(2) Increasing size of the solute displaces the composition of γ phases in the direction of lower electron concentration (as in the case of β phases). No γ phases are formed at all when the atomic size difference exceeds 20 per cent.

(3) Increasing electrochemical difference results in displacing the composition of the γ phase to higher electron concentrations. In the systems Cu-Zn, Cu-Ga, and Cu-Al, the compositional range of the γ phase lies almost entirely on the high electron concentration side of the 21/13 ratio.

The electron compounds of highest solute content are the 7/4 type, which have close-packed hexagonal structures. Like the γ structures, these are invariably brittle and are of no industrial or engineering importance, nor have they yet been analyzed in the same detail as the β and γ structures.

Ternary systems also show electron compounds which follow the same electron-to-atom ratios holding for binary systems. In some cases, atoms of a third element may be substituted for the solute in a binary compound without affecting the structure. At present, little work has been published on the theoretical background of ternary alloys of copper-base systems.

TABLE 22-1. ELECTRON COMPOUNDS IN COPPER-BASE BINARY SYSTEMS

3/2 Compounds			21/13 Compounds	7/4 Compounds
β — b.c.c.	ζ — c.p.h.	β Mn	γ — Complex Cubic	ε — c.p.h.
CuZn			Cu_5Zn_8	$CuZn_3$
CuBe			Cu_5Cd_8	$CuCd_3$
Cu_3Al			Cu_9Al_4	Cu_3Sn
Cu_3Ga			Cu_9Ga_4	Cu_3Ge
Cu_3In			Cu_9In_4	Cu_3Si
Cu_5Sn	Cu_5Ge	Cu_5Si	$Cu_{31}Si_8$	
			$Cu_{31}Sn_8$	

THE PHASE DIAGRAMS OF THE BINARY SYSTEMS

Cu-Ag[6]

Although Cu and Ag are both face-centered cubic univalent metals in the IB subgroup of the periodic table, the two elements differ in atomic size by 12 per cent. The difference appears to be too great for the formation of a continuous solid solution. The diagram is known with unusual accuracy. Lattice dimensions are[8]:

Cu	β, 8.0% Ag	α, 92% Ag	Ag
3.608 kX	3.633 kX	4.029 kX	4.077 kX

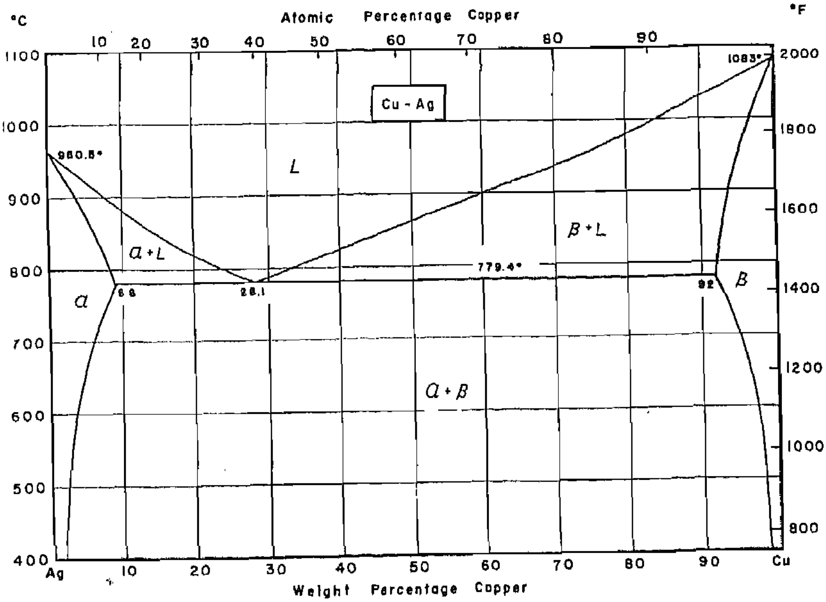

FIGURE 22-1. Diagram of the copper-silver system.

Cu-Al[9]

The β phase is an electron compound with the nominal composition Cu_3Al and a corresponding electron concentration of 3/2. It has a body-centered cubic structure with $a = 2.94$ kX.

The χ phase, which decomposes eutectoidally at 963°C, includes the composition Cu_9Al_4 of 15.9 weight per cent Al. This corresponds to the electron compound 21/13, which usually has the complex cubic γ-brass structure.

The γ_1 and γ_2 phases also include the Cu_9Al_4 composition at least from 800 to 500°C, and although at room temperature γ_2 contains more aluminum than that required by the 21/13 electron compound, the phase has the normal γ-brass structure with $a = 8.7$ kX. The excess of aluminum atoms in the structure may be taken as additional evidence that aluminum atoms are only partially ionized in these structures.

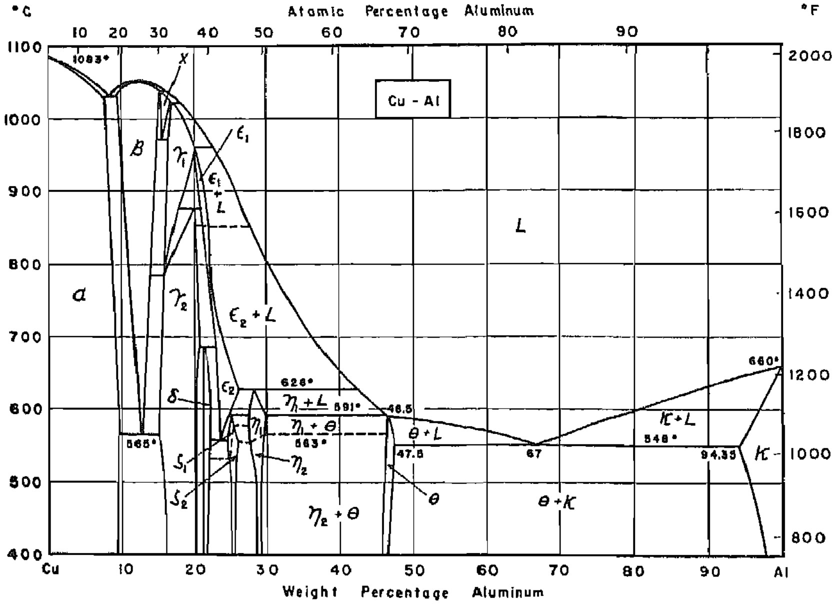

Figure 22-2. Diagram of the copper-aluminum system.

In the range of compositions 20 to 30 per cent Al, the equilibrium relations are complex and not yet fully understood. The ε, ζ, and η phases all show transformations which here are dashed and may represent ordering of the structure. The ε phase is cubic, the ζ phase is hexagonal, and the η phase is orthorhombic. The θ phase is tetragonal, with 8 Al and 4 Cu atoms per cell, $a = 6.04$ kX and $c = 4.86$ kX.

Important alloys for industrial use are found at each end of the diagram. At the aluminum end, the solid solution indicated here as the κ phase shows a decreasing solubility for copper, which is the basis for the major high-strength aluminum alloys, heat treated for precipitation hardening. Lattice dimensions of the κ (Al-rich) solid solutions are as follows:

Wt. Per cent Cu	0	1	2	3	4	5
Lattice edge, kX	4.0414	4.0393	4.0372	4.0350	4.0329	4.0308

When θ precipitates at low temperatures, *e.g.*, 100 to 200°C, from supersaturated α, the θ phase does not have its normal dimensions but instead has $a = 5.7$ and $c = 5.8$ kX. It is distorted to maintain a coherent interface between its basal plane and the cube plane of the α. The coherency distortions appear to be the chief source of precipitation hardening.

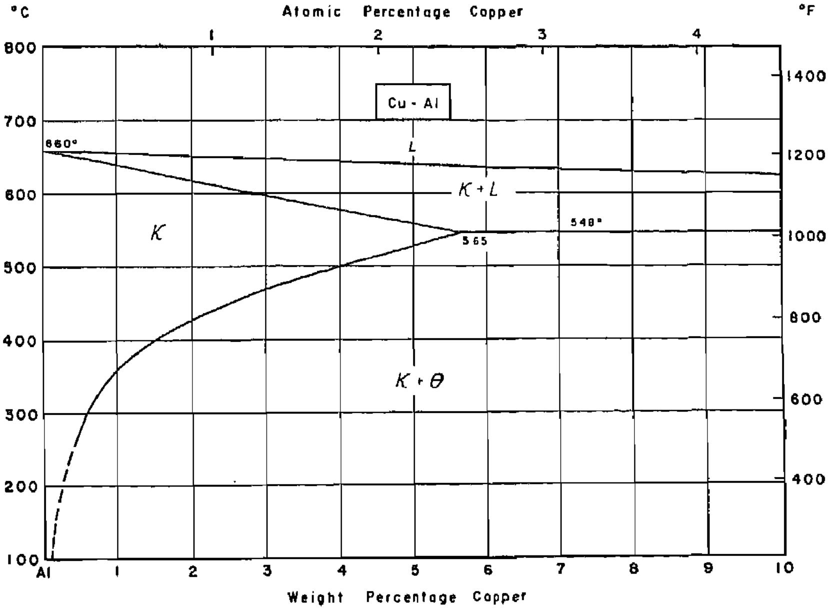

FIGURE 22-3. The aluminum-rich end of the copper-aluminum system; precipitation-hardening alloys.

Heat-treatable alloys at the copper-rich end of the diagram are those which consist of the β phase at high temperatures. Upon cooling, the β phase may transform to a number of metastable transition structures[10]. The regular C-type isothermal transformation diagram, comparable to that of the austenite of steel, is found for the β phase. Compositions near the eutectoid, 11.8 per cent Al, transform eutectoidally to $(\beta + \gamma_2)$ in a pearlitic aggregate when β is cooled and held isothermally in the range 565 to 420°C or when slowly cooled at a rate of 1°C per minute or less.

Rapid cooling of the β phase suppresses the eutectoid reaction but the body-centered cubic β phase begins to order at around 500°C and the ordered structure is called β_1. Ordering is not suppressed by rapid cooling although the temperature interval required for its completion is not known. At still lower temperatures, the ordered β_1 transforms to a martensite called β' for alloys with less than 13 per cent Al and γ' for alloys with more than 13 per cent Al. While both β' and γ' are close-packed hexagonal structures, the two differ both in x-ray pattern and micrographic appearance. The lattice constants of a 13½ per cent Al martensite, γ', are: $a = 2.606\text{Å}$, $c/a = 1.619$. These changes may be summed up as:

$$\begin{tikzcd}
& & \beta_1 \text{ (Al rich)} \arrow[r] \arrow[dr] & \alpha + \gamma_2 \text{ (isothermally)} \\
& & & \gamma' \text{ (cooling)} \\
\beta \arrow[r] & \beta_1 \arrow[uur] \arrow[dr] & & \\
& & \beta_1 \text{ (Al depleted)} \arrow[r] \arrow[dr] & \alpha + \gamma_2 \text{ (isothermally)} \\
& & & \beta' \text{ (cooling)}
\end{tikzcd}$$

Cu-As[6]

The form of this diagram for arsenic contents greater than 28 per cent is uncertain. Evidence concerning the γ phase is contradictory. The β phase represents the valency compound Cu_3As and probably it does not cover as wide a range of compositions as shown by the dashed boundaries. The limits of the α solid-solution field are based on x-ray studies[11]. Arsenic, which has a rhombohedral-type structure, expands the lattice of copper in the α solid-solution field as follows:

Wt. Per cent As	0	1.85	3.10	4.35	6.51	7.31	9.76
Lattice edge, Å	3.608	3.165	3.621	3.626	3.635	3.638	3.641

Cu-Au[6]

Copper and gold are both IB elements in the periodic table, are both face-centered cubic in structure, and form a series of continuous α solid solutions at high temperatures. However, the atoms differ in size by 11 per cent and the resulting tendency toward a eutectic results in a pronounced minimum in the liquidus-solidus curves. At low temperatures, the α solid solution becomes ordered with the designation α' or Cu_3Au as an ideal designation and α'' or CuAu. The layer-like structure of α'' with Cu atoms at 000 and 1/2,1/2,0 and gold at 0,1/2,1/2 and 1/2,0,1/2

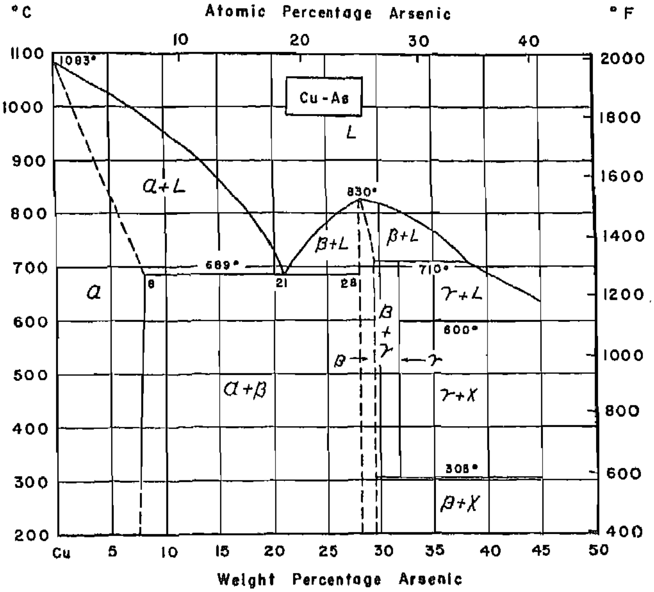

Figure 22-4. Diagram of the copper-arsenic system.

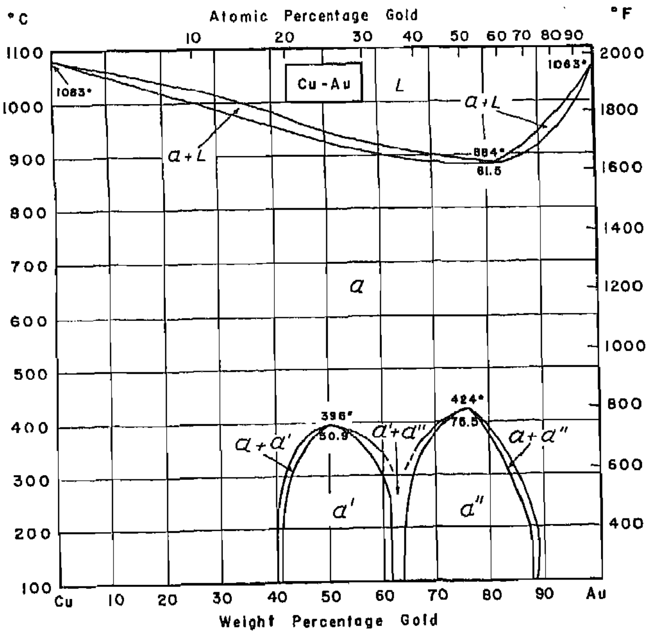

Figure 22-5. Diagram of the copper-gold system.

positions (or vice versa), results in a face-centered tetragonal lattice. Ordering in this system is definitely of the heterogeneous reaction type with alloys going through a two-phase field, $\alpha + \alpha'$ or $\alpha + a''$, for compositions on either side of the ideal Cu_3Au or CuAu. Ordering results in the usual changes of specific heat and electrical conductivity, the appearance of superstructure lines and, in the case of the tetragonal α'', pronounced hardening[12].

Lattice Parameters of Alloys Quenched from 600°C

Wt. Per cent Au	0	20	40	60	80	100
Lattice edge, kX	3.608	3.655	3.709	3.785	3.894	4.070

Tetragonal α (CuAu); $a = 3.956$ kX; $c/a = 0.926$

Cu-Be[13]

This diagram is well established except for the compositional limits of the δ phase. Three intermediate phases are found. The β phase is a disordered body-centered cubic structure with $a_0 = 2.72$Å at 620°C. The γ phase, which at high temperature includes the composition of CuBe, is an ordered body-centered cubic structure of the CsCl type and could be classified as an electron compound of the 3/2 class. For this reason, it is sometimes called a β' phase, analogous to β' of the Cu-Zn system. The δ phase is cubic with a $CuMg_2$ type of structure (the δ field includes the composition $CuBe_2$).

The most recent research on the β eutectoid reaction, $\beta \rightarrow \alpha + \gamma$[14], shows that the true reaction temperature is 608°C rather than 575. Isothermal reaction studies show the eutectoid reaction rate is most rapid at 500°C and that the reaction product is a pearlitic aggregate of α and γ. Rapid quenching can retain the β phase to room temperature and a subsequent martensitic reaction at sub-zero temperatures is possible.

Cu-Bi[7]

The system is marked by unusual shapes of the hypoeutectic liquidus and solidus lines. The maximum solubility of Bi in α at around 850°C is logically related to observations of hot shortness in copper containing small quantities of bismuth[15]. The maximum in solubility is observed to occur between the melting point of a substance and the eutectic temperature only when the eutectic temperature is very low as compared to the melting point of the solvent, as in this case. The diminished amplitude of thermal vibration at lower temperatures is believed to prevent the solubility from increasing in the usual way down to the eutectic temperature.

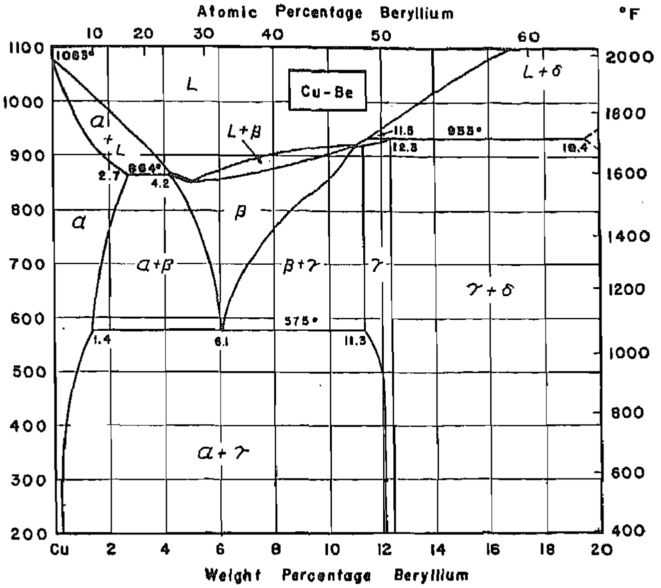

FIGURE 22-6. Diagram of the copper-rich end of the copper-beryllium system; alloys up to 2.2 per cent beryllium are heat treated for precipitation hardening.

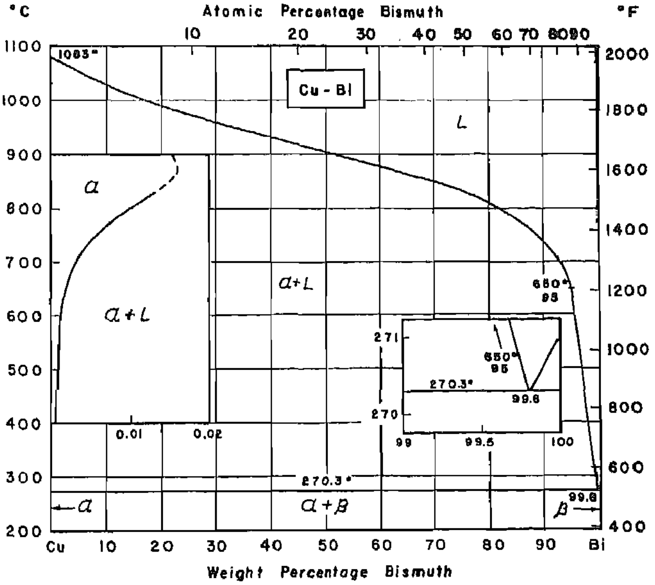

FIGURE 22-7. Diagram of the copper-bismuth system.

Cu-C

It is not known whether this system is of the eutectic or peritectic type. The solubility of carbon in liquid copper[16] is of interest principally because of the relation to reactions when carbon-containing copper is exposed to oxidizing gases during refining operations.

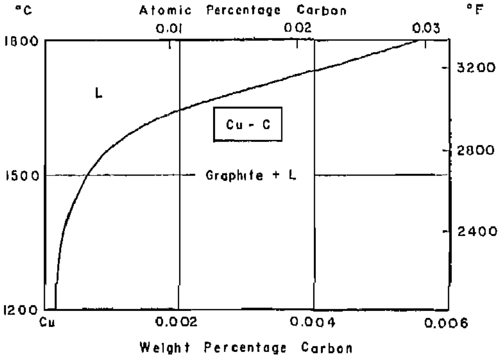

FIGURE 22-8. Diagram of the copper-carbon system up to 0.006 per cent carbon.

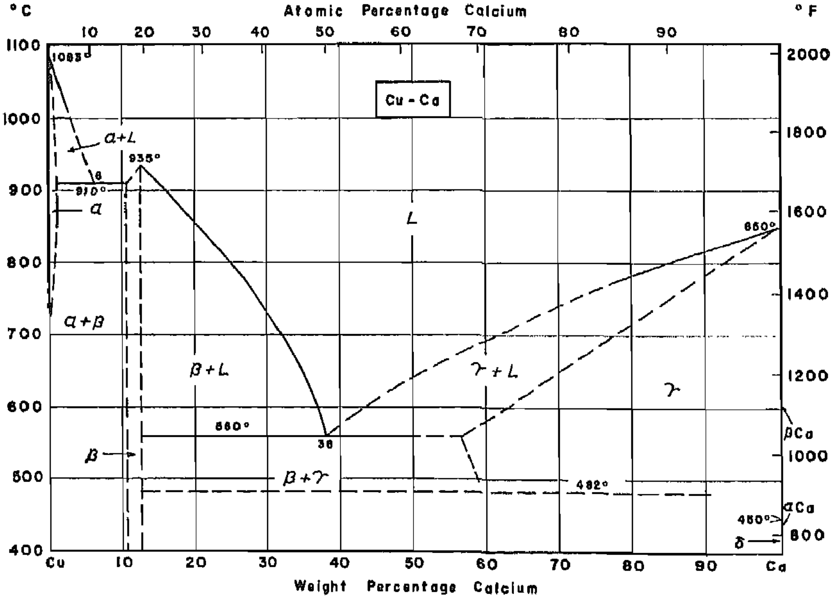

FIGURE 22-9. Diagram of the copper-calcium system.

Cu-Ca[6]

There are several uncertainties in this diagram, particularly at the calcium-rich end. The β phase is Cu_5Ca and has a hexagonal structure with $a_0 = 5.097$ kX and $c/a = 1.579$[17]. The solubility of calcium in solid copper or α is less than 0.1 per cent at room temperatures.

Cu-Cd[7]

The alloys with cadmium, an element in the IIB subgroup of the periodic table, are in several respects analogous to those with zinc.

Data on the four intermediate phases are:

(1) β corresponds to Cu_2Cd and, with a very narrow compositional range, it appears to be a valency compound.

(2) γ corresponds to Cu_4Cd_3. It does not appear upon solidification even at very slow rates, but forms only after prolonged annealing near 500°C. Slow cooling of the liquid results in a metastable eutectic, $L \rightarrow \beta + \delta$, at 540°C.

(3) δ is a 21/13 electron compound of the γ-brass structure, complex cubic of 52 atoms with four groups of Cu_5Cd_8 per unit cell and $a_0 = 9.635$ kX[19].

(4) ε corresponds to $CuCd_3$ and is also an electron compound of the 7/4 ratio type. Like β_1 it has an extremely narrow range of solid solubility.

The solidus line for the α solid-solubility field shows a maximum solubility above the β peritectic temperature of 549°C[18]. This resembles the Cu-Bi system and is not unusual in systems with very pronounced lowering of the solvent melting point. The solid solubility of Cd in α decreases from 3.7 at 549°C to less than 1 per cent at 300°C. The solid solubility of Cu in Cd is between 0.005 per cent and 0.01 per cent at 270°C.

Cu-Ce[7]

There apparently have been no new investigations of this system. The absence of solid solubility as shown at the termini of the system and for the several compounds Cu_6Ce, Cu_4Ce, Cu_2Ce, and CuCe cannot be taken as necessarily accurate.

Cu-Co[6]

Some investigators have found a biliquidus field from 32 to 72 per cent Co. In this range, the liquidus is quite flat and probably the presence of impurities causes the formation of two liquids. The analogous effect is found in the Cu-Fe system where the presence of carbon in alloys causes two liquids to form. The solubility of copper in β cobalt is known only approximately and the effect of copper on the $\beta \rightleftharpoons \alpha$ transformation of cobalt at 420°C is unknown.

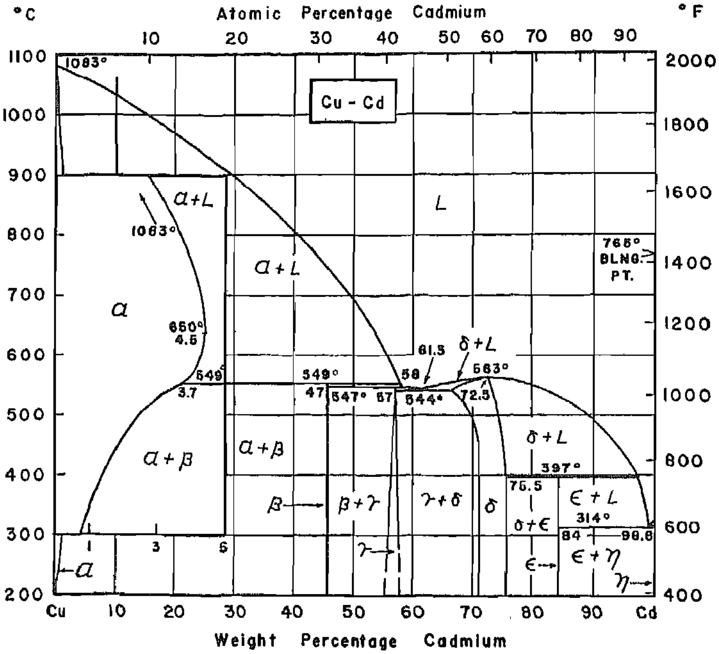

FIGURE 22-10. Diagram of the copper-cadmium system.

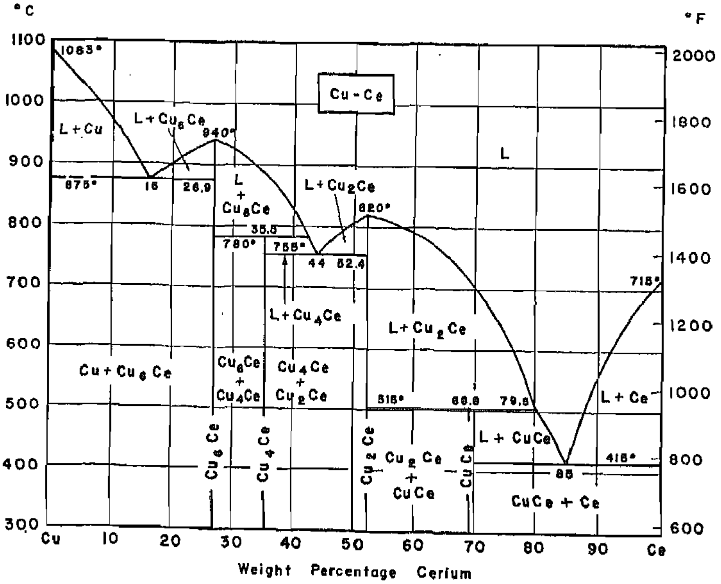

FIGURE 22-11. Diagram of the copper-cerium system.

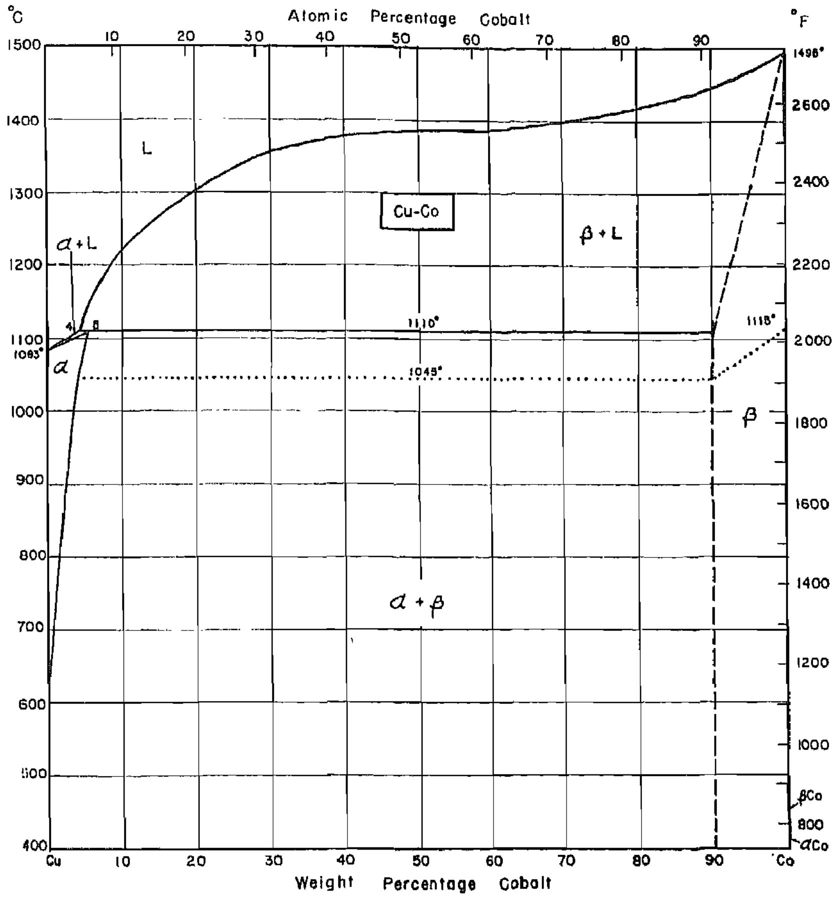

FIGURE 22-12. Diagram of the copper-cobalt system.

Cu-Cr[7]

The solid solubility of Cr in Cu is well established now as 0.7 per cent at the eutectic temperature. Alloys containing 0.2 to 0.6 per cent Cr show age hardening upon quenching from 1050°C and reheating in the range 400 to 600°C[20]. The precipitated Cr phase (β) impedes grain growth in copper alloys containing chromium in the above range of 0.2 to 0.6 per cent.

Cu-Fe[7]

The biliquidus field which approaches but does not appear to meet the liquidus is observed apparently only in the presence of carbon in the alloys. In the absence of carbon, all alloys can be prepared in homogeneous form and hot and cold worked[21]. Most interest centers in the α solid-solubility limits at each end of the diagram. There is some disagreement about the solubility of Cu in α Fe at the eutectoid temperature. X-ray data[22], which are generally preferred, show the maximum solubility to be 1.4 per cent Cu at the eutectoid temperature of 850°C, decreasing to 0.4 per cent at 600°C. The lattice parameter of α Fe, 2.8607Å, is increased to 2.8625Å at saturation with 1.4 per cent Cu. The age hardening of iron, or low-carbon steel, containing 1.0 to 1.5 per cent Cu makes it possible to obtain increased strengths in heavy sections where quench hardening would be impossible or expensive in high-hardenability alloying elements. However, alloys of all compositions in the system can be fabricated. Those with from 5 to 10 per cent Cu, quenched from 950°C and aged at 450°C, show maximum strength. Wires of 45 and 55 per cent Fe, made from Mg-deoxidized metal, show excellent combinations of strength and ductility[21].

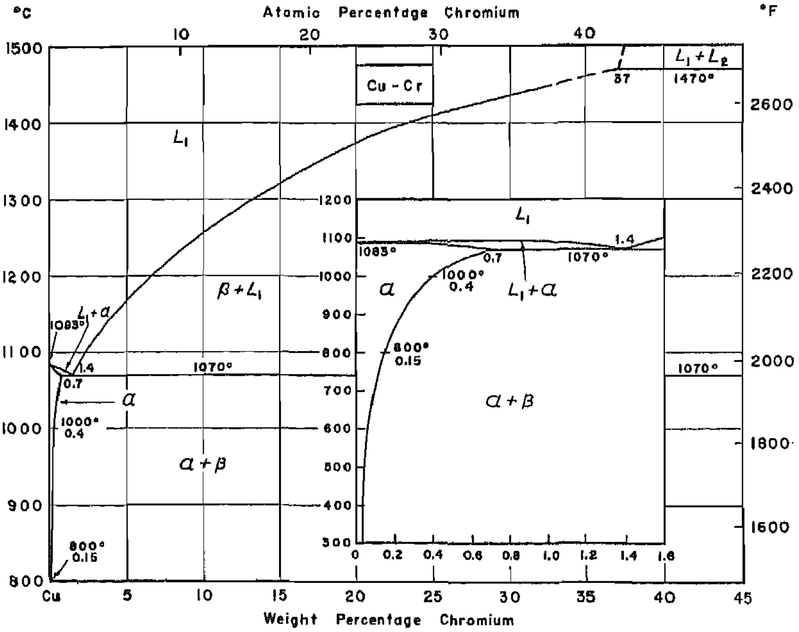

FIGURE 22-13. Diagram of the copper-chromium system up to 45 per cent chromium.

Cu-In

Indium forms the usual electron compounds with copper. β is a body-centered cubic structure of the 3/2 electron type although its compositional field does not quite extend to the required 25 atomic per cent, or Cu_3In. γ is a complex cubic structure of the γ-brass type with a lattice constant of 9.2317 kX. The compositional range just barely includes the Cu_9In_4 compound required for the 21/13 electron ratio of γ structures. The γ phase changes to δ, which is a tetragonal distortion of the γ phase with $a = 8.97$ and $c = 9.14$ kX[23]. The η phase would include the composition Cu_5In_3, representing a 7/4 electron compound. This phase has the normal NiAs structure, *i.e.*, the Cu atoms occupy simple hexagonal lattice positions with the In atoms in intermediate layers.

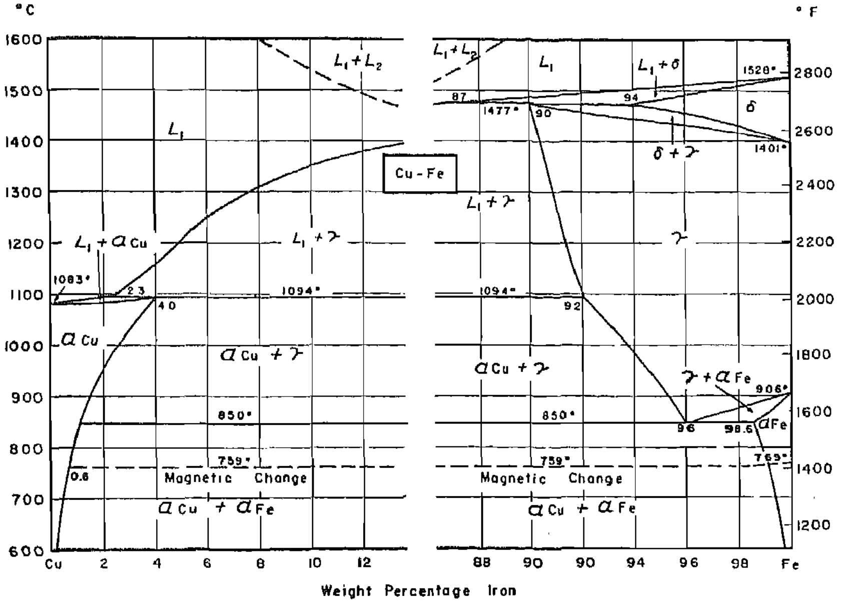

FIGURE 22-14. Diagram of the copper-iron system.

Cu-La[7]

Like the Cu-Ce system, this one shows several compounds[24], *e.g.*, Cu_4La and Cu_3La, of unknown structure. Since there has been no recent work on the system, the indicated lack of solid solubility at the copper end of the system or for the compounds may or may not be accurate.

Cu-Li[7]

There is no detectable solubility of lithium in solid copper or of copper in solid lithium[25]. The eutectic composition is very close to 100 per cent Li and the eutectic melting point must be only very slightly below the melting point of pure lithium. The shape of the liquidus and the low melting point of the eutectic would suggest that the maximum solubility of Li in Cu would occur well above the eutectic temperature (*cf.* the Cu-Bi system).

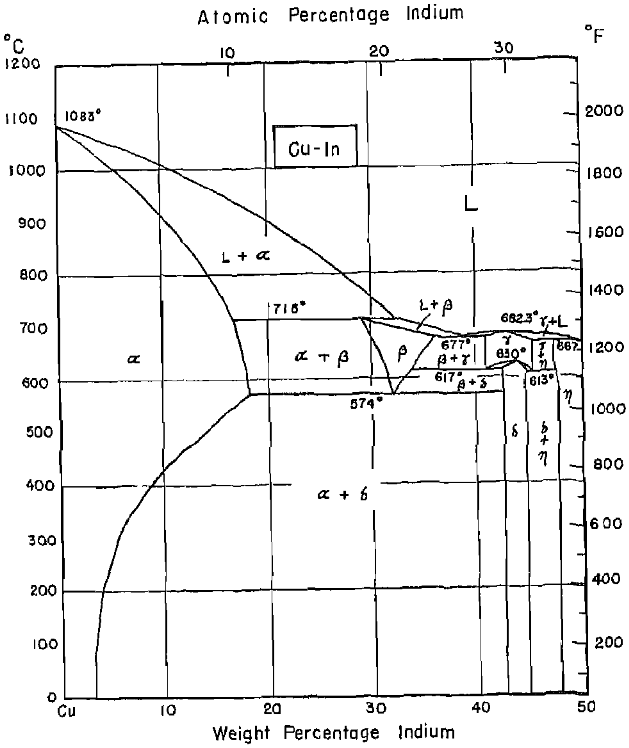

FIGURE 22-15. Diagram of the copper-rich half of the copper-indium system.

Cu-Mg[7]

Two intermediate alloy phases are formed in this system, β or Cu_2Mg and $CuMg_2$. The β phase is hexagonal with $a_0 = 5.281$ kX and $c_0 = 3.464$ kX. $CuMg_2$ is a face-centered cubic structure with $a = 6.99$ kX. While Cu has some solubility in Mg, its effect on the parameter values of Mg are too small to be measured[26]. However, it is claimed elsewhere[6] that the solubility in Mg, rather than being about 0.03 per cent Cu as shown here, is 0.55 per cent Cu at the eutectic and 0.20 per cent at 300°C.

Cu-Mn[6]

Manganese exists in three well-defined different allotropic forms. α is complex cubic with 58 atoms per cell and has nearly zero solubility for

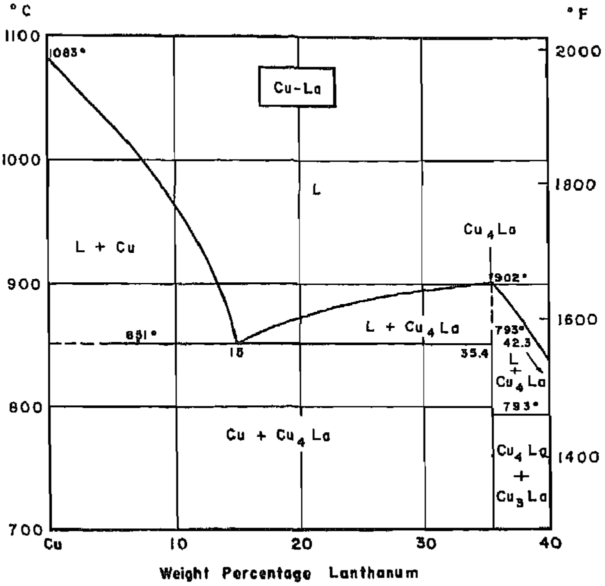

FIGURE 22-16. Diagram of the copper-lanthanum system up to 40 per cent lanthanum.

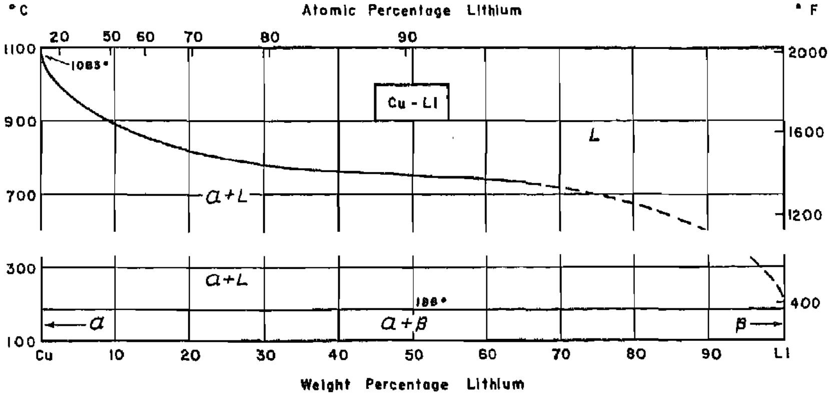

FIGURE 22-17. Diagram of the copper-lithium system.

copper. β is complex cubic with 20 atoms per cell and also will not dissolve an appreciable amount of copper. γ is simple face-centered tetragonal at room temperature when retained by quenching. It has nearly the same effective atom size as copper so that it forms a continuous series of solid solutions. The liquidus:solidus lines converge at a minimum. As the manganese content of γ (normally called α at the copper-rich end), increases above 83 per cent, the structure of quenched alloys gradually changes from face-centered cubic to face-centered tetragonal. However, high-temperature x-ray studies show the structure is always face-centered cubic within the γ field[28]. The existence of the δ form of manganese is apparently established although the limits of the $\delta \rightleftharpoons L + \gamma$ reaction have not been defined.

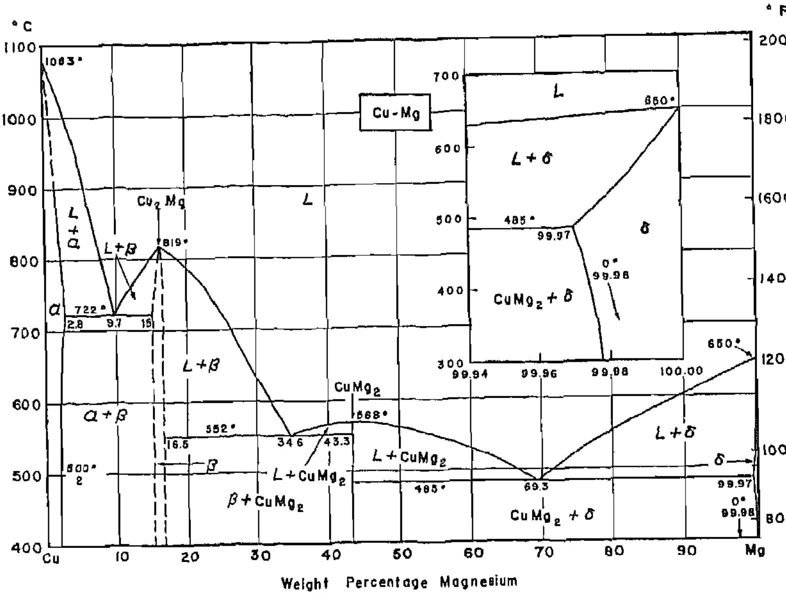

FIGURE 22-18. Diagram of the copper-magnesium system.

GAMMA-PHASE LATTICE PARAMETERS, QUENCHED ALLOYS[27]

Wt. per cent Mn	0	10.8	20.1	30	40	50
Lattice edge, Å	3.608	3.658	3.688	3.714	3.735	3.745
Wt. per cent Mn	60	70	80	89.2	94	100
Lattice edge, Å	3.754	3.752	3.747	3.761	3.767	3.774
c/a	1.0	1.0	1.0	0.963	0.950	0.938

Cu-Ni[6]

Since copper and nickel are adjacent in the periodic table, are electrochemically similar, have atoms of nearly the same size in the solid state (within 2 per cent), and are both face-centered cubic, they form a continuous series of solid solutions. The lattice parameters of alloys vary linearly according to Vegard's law. No ordering of the solid solution has been detected although anomalies in electrical resistivity coefficients are observed in alloys in the vicinity of 50 per cent Ni.

The Curie temperature varies linearly with nickel content, from 353°C for pure Ni to −170°C at the 50 per cent nickel concentration.

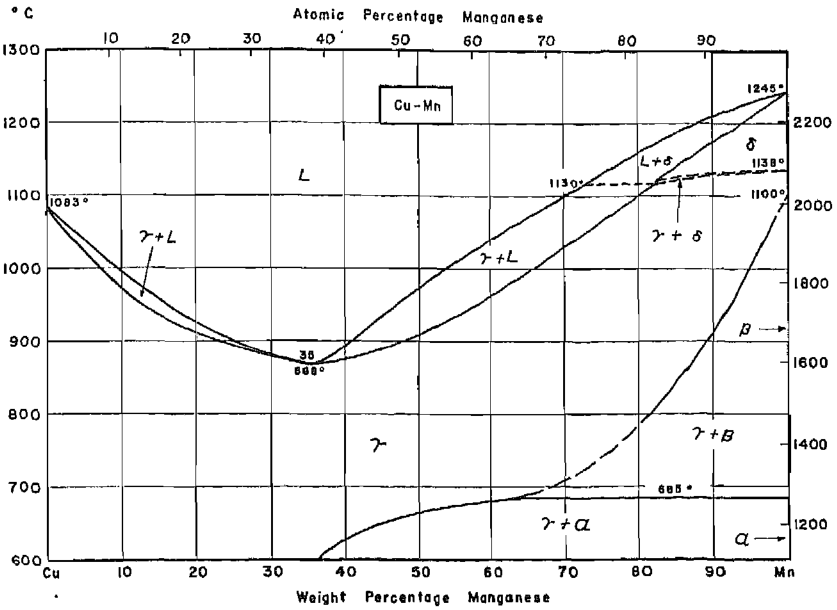

FIGURE 22-19. Diagram of the copper-manganese system.

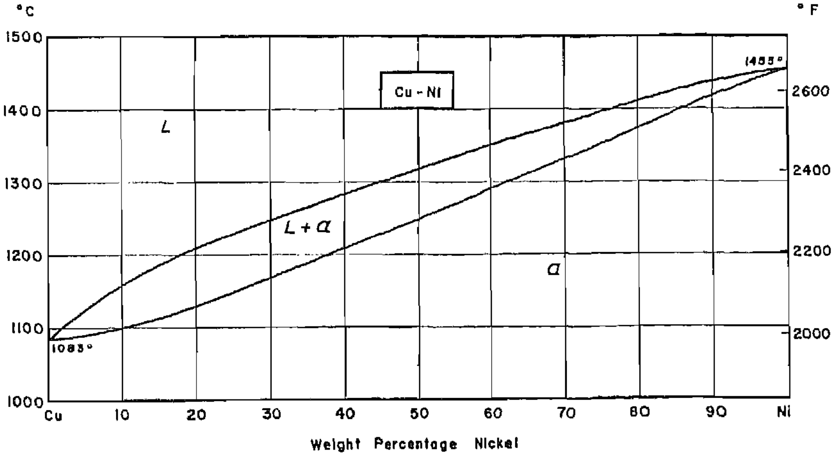

FIGURE 22-20. Diagram of the copper-nickel system.

Cu-O[7]

The solid solubility of oxygen in copper depends greatly on the purity of the copper and may be doubled by the presence of iron as impurity. This explains some of the contradictory data in the literature[29]. Cuprous oxide decomposes eutectoidally, under equilibrium conditions, at about 375°C to α and CuO. In solid alloys, pressure and other factors prevent this reaction so that oxide inclusions in copper are always Cu_2O rather than CuO.

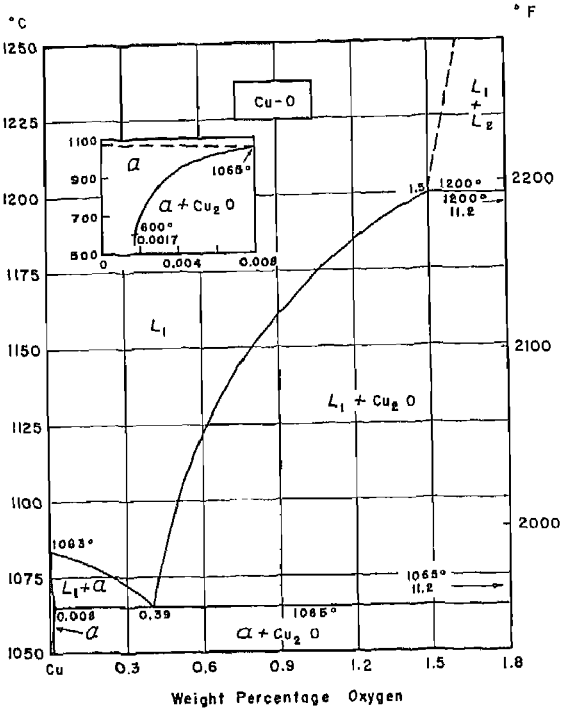

FIGURE 22-21. Diagram of the copper-oxygen system up to 1.8 per cent oxygen.

Cu-P[6]

The β phase in this system is a valency compound, Cu_3P. Other compounds are formed at higher phosphorus concentrations, but these are unstable at elevated temperatures and decompose.

Most interest in this system arises from the use of phosphorus as a deoxidizer of copper and its alloys. For this reason, the α solubility field and the effect of residual phosphorus on conductivity are of concern. The effect of phosphorus in solid solution on the lattice parameter of copper is as follows[11]:

Per cent P	0	0.58	1.0	1.60
Lattice edge, Å	3.6077	3.6092	3.6101	3.6117

The effect of phosphorus on conductivity, in the absence of oxygen, is severe, with 0.73 per cent IACS drop of conductivity for each 0.001 per cent P.

Cu-Pb[6]

The maximum solid solubility of lead in copper is of the order of 0.002 to 0.005 per cent at the monotectic temperature of 953°C. The horizontal at 326°C represents a eutectic reaction. The eutectiferous liquid contains only 0.06 per cent Cu and the lead-rich solid solution, β in this diagram, contains less than 0.007 per cent Cu.

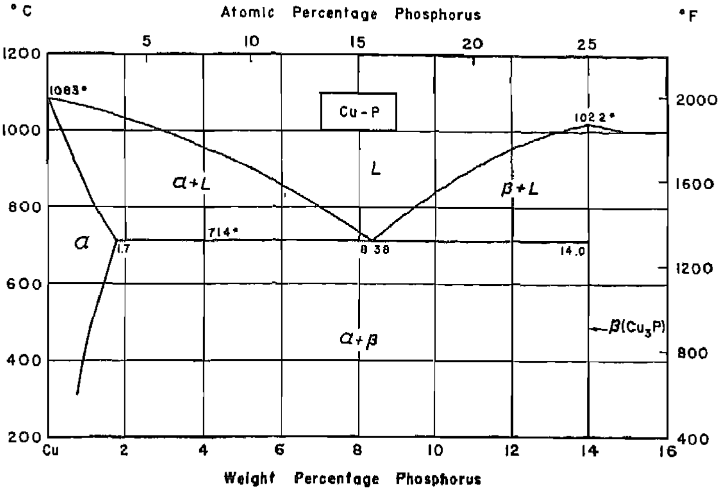

FIGURE 22-22. Diagram of the copper-phosphorus system up to 16 per cent phosphorus.

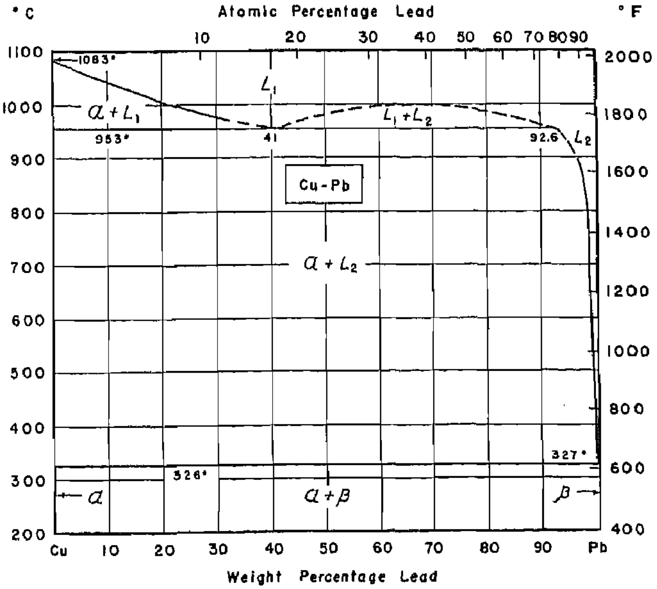

FIGURE 22-23. Diagram of the copper-lead system.

Cu-Pd[6]

Palladium is a face-centered cubic metal with an effective atom diameter only 7 per cent greater than copper; hence it forms a continuous series of solid solutions at elevated temperatures. However, ordering of the α solid solution takes place analogously to the Cu-Au system. The β phase is of the CuPd type, although it does not include the equiatomic composition. β is an ordered body-centered cubic structure. The outline of the β field conforms to classical phase-change requirements.

At lower concentration in the area designated here as α', which includes the Cu_3Pd composition, an ordered tetragonal structure is found[30] with 36 atoms per cell, $a = 9.741$Å and $c = 7.312$Å. From 10 to 18 atomic per cent Pd, an ordered face-centered cubic structure called here α'' is found. It is probable that the ordering reactions for α' and α'' should be represented as phase changes with fields of $(\alpha + \alpha')$ and $(\alpha + \alpha'')$ appearing in the diagram.

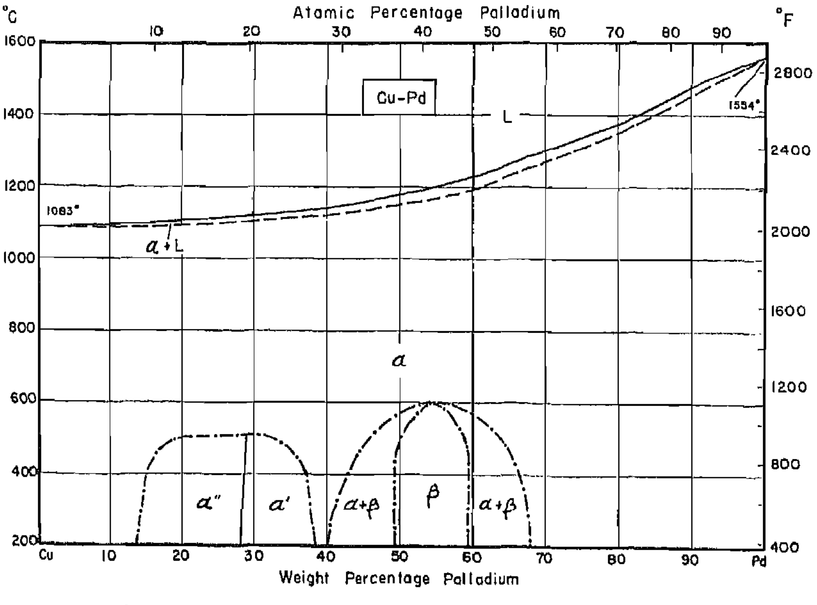

FIGURE 22-24. Diagram of the copper-palladium system.

Cu-Pt[6]

Platinum is a face-centered cubic metal with an effective atomic diameter only 8 per cent greater than that of copper. It forms a continuous series of solid solutions at elevated temperatures. Like the Cu-Au and Cu-Pd systems, ordering of the α solid solutions occurs at lower temperatures[31]. The α' designates an ordered face-centered cubic structure of the Cu_3Pt type with a pronounced tolerance for extra copper atoms. The α'' structure, of CuPt, is reported to show trigonal symmetry. It is probable that a careful study of the system would show $(\alpha + \alpha')$ and $(\alpha + \alpha'')$ fields on either side of these ordered structure phases.

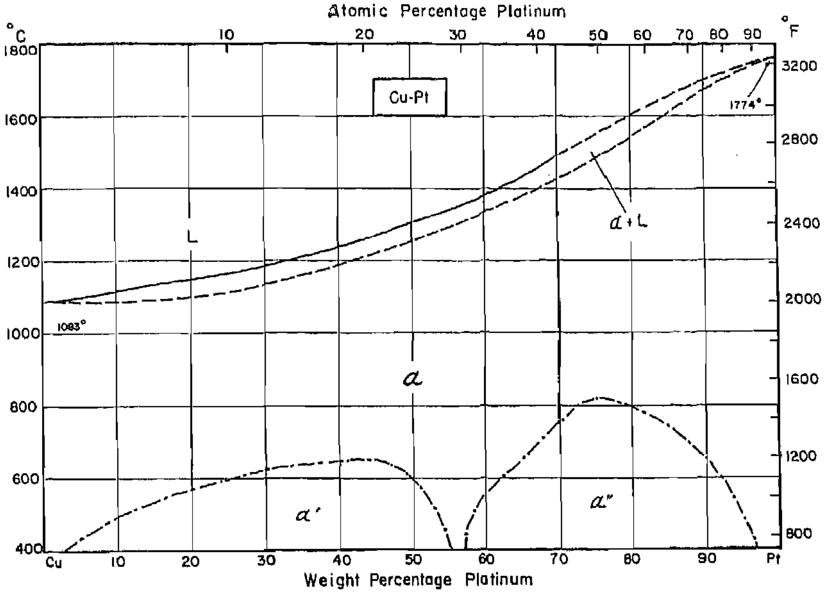

FIGURE 22-25. Diagram of the copper-platinum system.

Cu-S[7]

Copper forms the normal valency compounds with sulfur, although the diagram reproduced here shows only the copper-rich end and does not carry up to the first compound, Cu_2S at 20.2 weight per cent S. At the monotectic temperature of 1103°C, the second liquid contains 17.9 per cent sulfur. The solid-solubility limits of sulfur in α are based on electrical conductivity[32] data.

Cu-Sb[6]

The diagram shown is that of Shibata and associates[33]. The α solid-solubility field in this diagram may be incorrect since x-ray data, while generally supporting the maximum given for the eutectic temperature, show a sharp decrease in solubility below the 400°C eutectoid with a solubility of only 2 per cent at 200°C[11].

Structural data on the various intermediate phases or compounds are as follows:

Phase	Wt. Per Cent Sb	Structure	Atoms per cell	a, kX	c, kX	c/a
α	0	F.c.c.	4	3.068		
α	10.2	F.c.c.	4	3.672		
γ	25.8	Orthorhombic	49	9.28	8.63	$b = 8.18$
δ	29.8	Hexagonal	12	10.836	8.611	0.795
ε	41.05	Hexagonal	15	5.495	8.686	1.581
β	43.29	B.c. tetragonal	$2n$	9.01	8.57	0.95
ζ	48.92	Tetragonal	12	5.62	6.07	1.081
η	100	Hexagonal	6	4.290	11.237	2.619

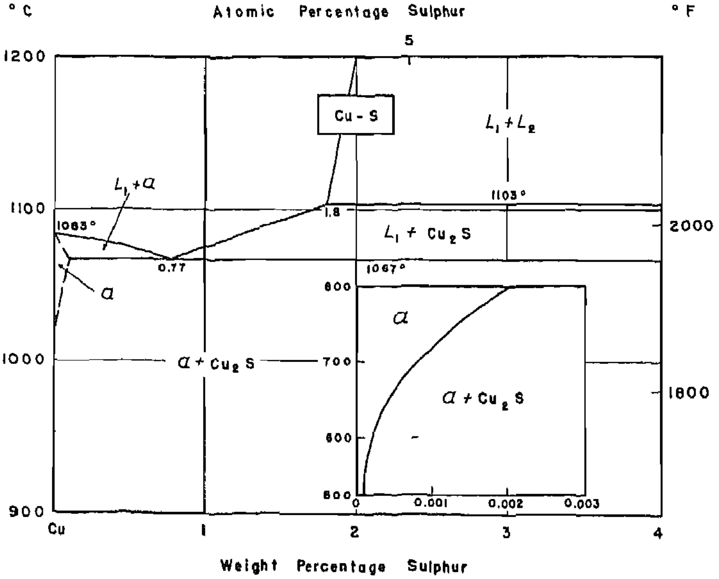

FIGURE 22-26. Diagram of the copper-sulfur system up to 4 per cent sulfur.

Cu-Se[6]

The β phase is a valency compound, Cu_2Se. It has a structural transformation at about 110°C and below this shows the cubic CaF_2 structure. In this case, the Se atoms would occupy the atom sites of a face-centered cubic structure with 8 copper atoms within the cell (at 1/4,1/4, 1/4; 1/4,1/4,3/4; 1/4,3/4,1/4; 1/4,3/4,3/4; etc.). There is another selenide, CuSe, not shown here, which melts peritectically at 700°C. The indicated solubility of Se in α is based on electrical conductivity measurements[32].

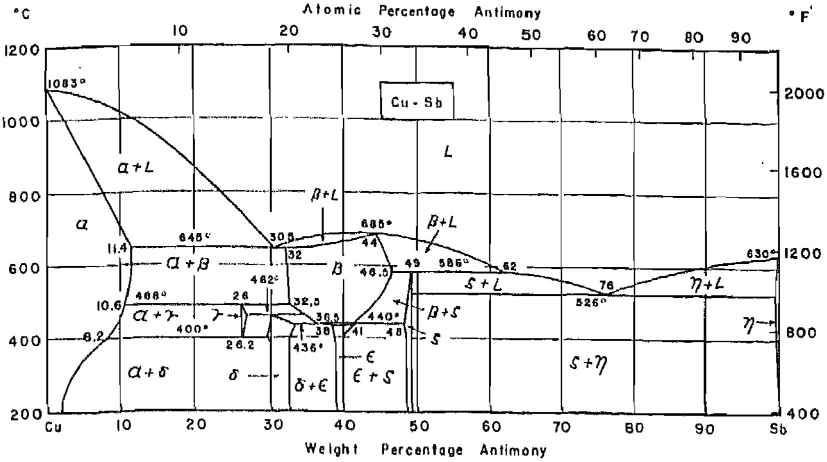

Figure 22-27. Diagram of the copper-antimony system.

Cu-Si[6]

The κ phase is very similar to α in lattice dimensions. Data in the table below show that the only difference is in stacking sequence. In α, stacking of atoms on (111) close-packed planes proceeds in intervals of three, A, B, C, A, B, C, ... In κ, stacking of atoms on the equivalent close-packed plane (0001) is in sequence $A, B, A, B, \ldots$. Cold working of supersaturated α produces unusually high strain hardening by the introduction of stacking faults in the α structure[31].

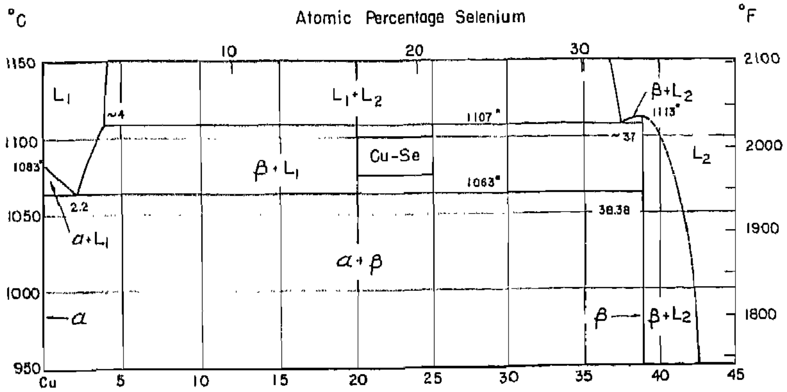

Figure 22-28. Diagram of the copper-selenium system up to 45 per cent selenium.

Phase	Wt. Per Cent Si	Structure	Atoms per cell	a, kX	c, kX
α	0	F.C.C.	4	3.6077	
α	4.65	F.C.C.	4	3.6139	
α	5.2	F.C.C.	4	3.6146	
κ	5.2	c.p. hex.	6	2.5539	4.1765
κ	5.65	c.p. hex.	6	2.5566	4.1737

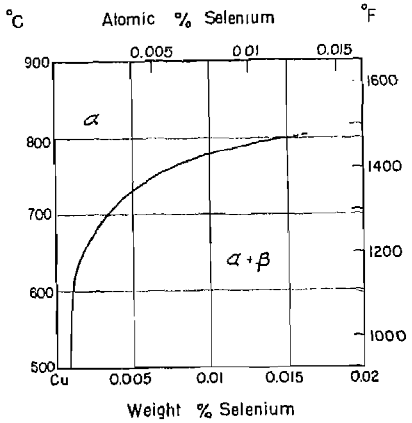

Figure 22-29. Enlargement of copper-selenium diagram for alloys below 0.02 per cent selenium.

The β phase is an electron compound with the nominal designation Cu_5Si or an electron concentration of 3/2. The ε phase is also an electron compound with the nominal designation $Cu_{31}Si_8$ to express the electron concentration of 21/13. The η phase is the third electron compound, with a nominal designation of Cu_3Si to express an electron concentration of 7/4. The last phase shown in the diagram, θ, is actually silicon, which presumably has almost zero solubility for copper.

Cu-Sn[35]

Copper forms a series of electron compounds with tin. The β phase, Cu_5Sn, is a compound of the 3/2 type with a body-centered cubic structure. The γ phase is an ordered body-centered cubic structure. In neither case does the phase persist to lower temperatures nor can β or γ be preserved by quenching. Quenched alloys show a series of complex metastable transition structures. The ε phase is the normal 7/4 electron compound or Cu_3Sn with an orthorhombic structure and η has the NiAs structure (*cf.* Cu-In).

The δ phase, formed from γ and ζ peritectoidally at 592°C, is the 21/13 electron compound with a composition of $Cu_{31}Sn_8$ and the regular γ-brass structure, *i.e.*, complex cubic. This phase at one time was con-

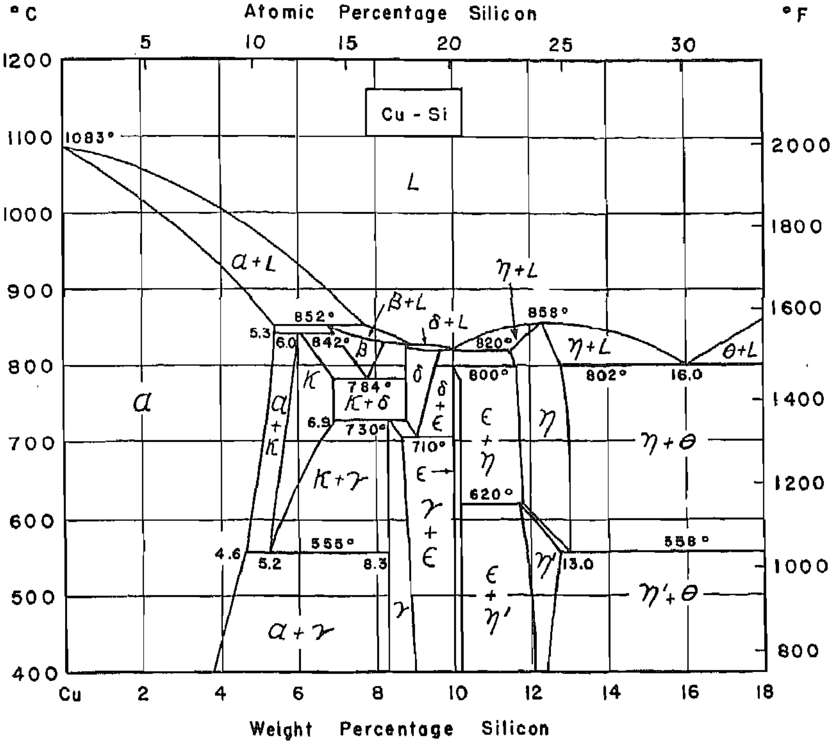

FIGURE 22-30. Diagram of the copper-silicon system up to 18 per cent silicon.

sidered stable down to room temperature since the eutectoid $\delta \rightarrow \alpha + \varepsilon$ is so sluggish that even after 63 days at 300°C, only about 5 per cent of the δ in a Cu:33 per cent Sn alloy had transformed. The product of the eutectoid reaction, when it occurs, is a pearlitic aggregate of $\alpha + \varepsilon$[36].

LATTICE STRUCTURES OF PHASES[37]

Phase	Wt. Per Cent Sn	Structure	a	c/a
α	0	F.C.C.	3.607Å	
α	15.5	F.C.C.	3.695	
γ	34	B.C.C.	17.92	
δ	32.5	γ brass	17.919	
ε	68	c.p. hex.	2.7504Å	1.5706
η	61	NiAs		

Cu-Te[6]

The β phase, Cu_2Te, is a valency compound and, instead of melting congruently as shown in this diagram, may undergo a peritectic reaction at 857°C. If the latter is true, then the 857°C horizontal should extend to the right to intersect the liquidus and the liquidus continue from there up to the 1055°C monotectic.

There are reported transformations of β to β' at 387°, of γ to γ' at 365°, and β' to β'' in the range 360 to 345°C. The evidence supporting the existence of these transitions is thermal analysis only and because of the uncertainties, the transformations have not been included in this diagram.

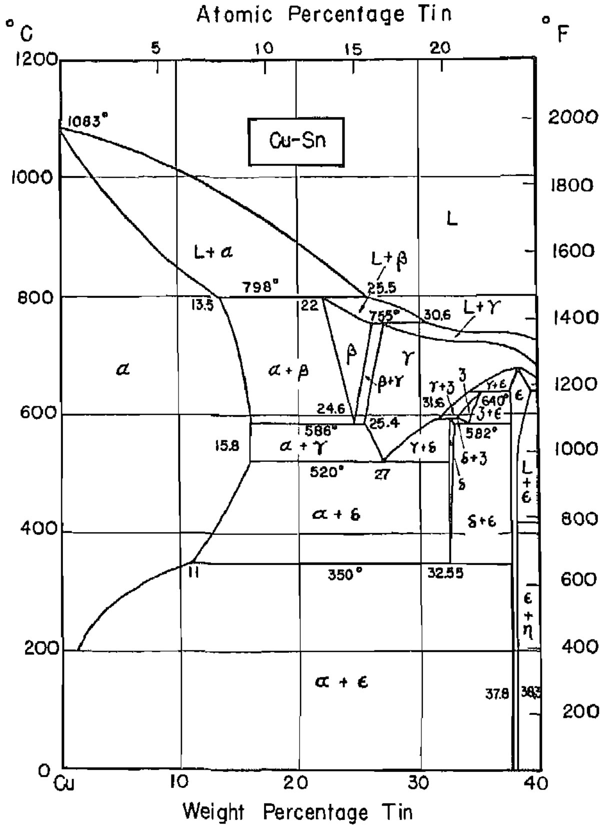

FIGURE 22-31. Diagram of the copper-tin system up to 40 per cent tin.

The indicated solid solubility of Te in Cu is based on electrical conductivity measurements[32]. Fortunately, Te has only a small effect on the conductivity of copper and has found some use as a hardener of copper conductors.

Cu-Th[7]

Copper forms three compounds with thorium, each melting congruently and showing a eutectic with the adjacent phase[33].

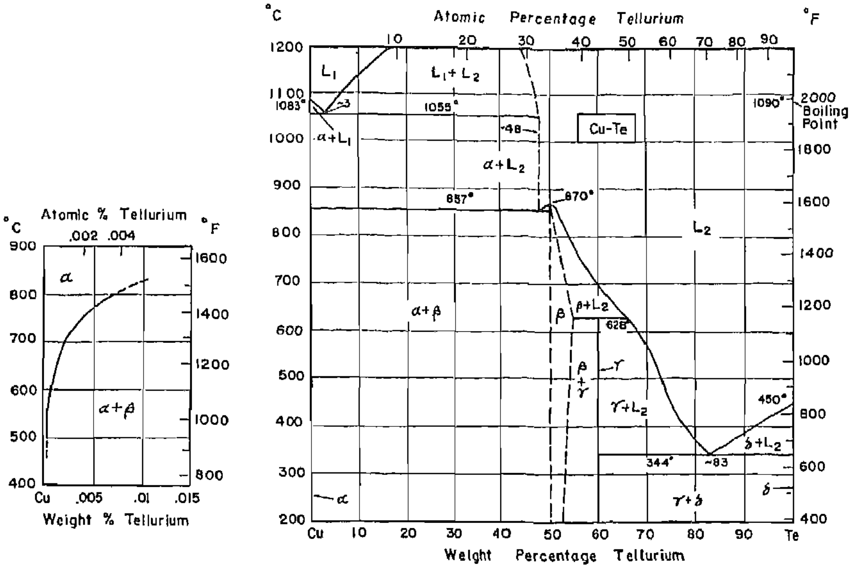

Figure 22-32. Diagram of the copper-tellurium system.

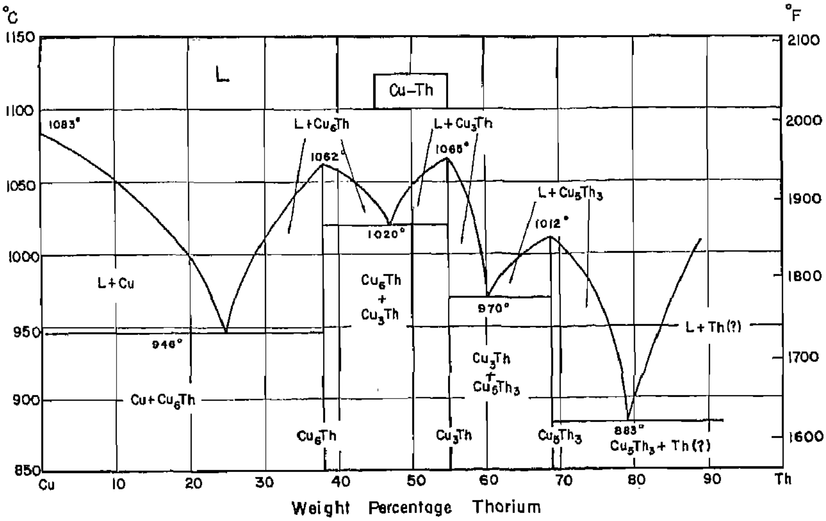

Figure 22-33. Diagram of the copper-thorium system.

Cu-Ti[6]

There appears to be a eutectic at about 24 per cent Ti between the α copper solid solution and an unknown copper-titanium compound. The indicated decrease in solubility of Ti in α is the basis of age-hardening characteristics which have as yet been of no industrial significance.

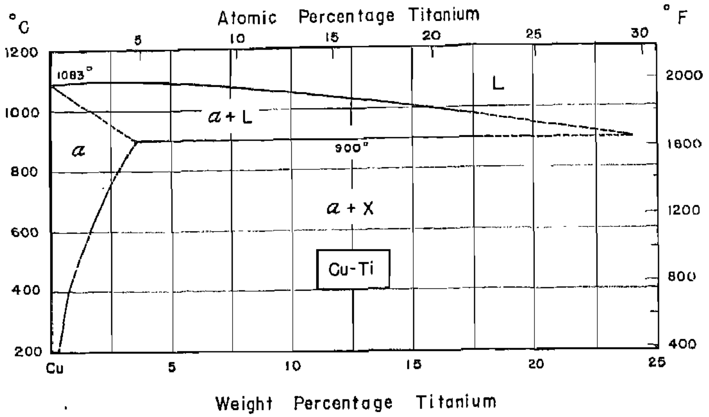

FIGURE 22-34. Diagram of the copper-titanium system up to 25 per cent titanium.

Cu-Tl[7]

Copper forms a monotectic with thallium. The thallium-rich liquid reacts peritectically at 302°C to form a Tl-rich solution, and a further solid-state transformation in the thallium is reported at 232°C[30].

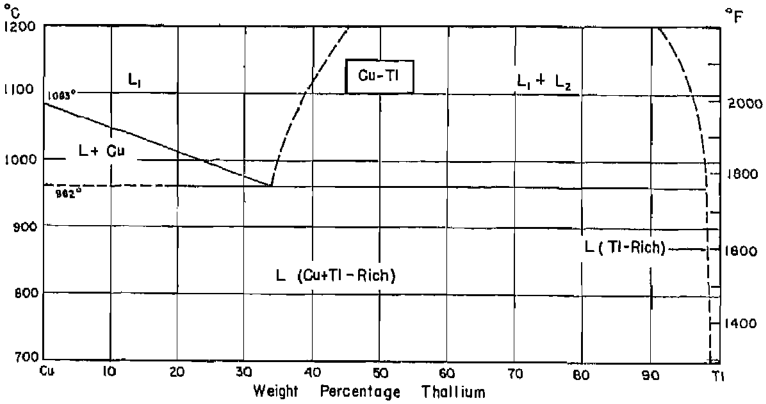

FIGURE 22-35. Diagram of the copper-thallium system.

Cu-Zn[40, 49]

The copper-zinc diagram shows a sequence of electron compounds, *viz*: β or CuZn, which is the 3/2 compound with a body-centered cubic structure; γ, which includes the Cu_5Zn_8 composition and is a 21/13 compound with a complex cubic structure; and ε, which nominally is $CuZn_3$, and has the 7/4 close-packed hexagonal structure.

The β phase in this system is preserved to room temperature but undergoes long-range ordering at 454 to 468°C (depending on zinc content) to form β′. Although the ordering reaction cannot be suppressed by even drastic quenching, quenching of β from the vicinity of the ordering reaction, *e.g.*, 455°C, results in abnormally high indentation hardness and a subsequent very slow rate of softening at room temperature. This is in contrast to quenching from 500°C, which gives a much softer structure to begin with and one which at room temperature further softens slightly at a rapid rate[41]. The energy change upon ordering is 9.8 cal per gram and there is an entropy change of approximately 0.0145 cal per gram[42]. There are the usual discontinuities in specific-heat curves and electrical conductivity associated with long-range ordering[42, 43]. While the β′ phase shows limited ductility at room temperature, it can readily be fabricated at 200 to 250°C, and then above 500° in the β form it is exceedingly plastic.

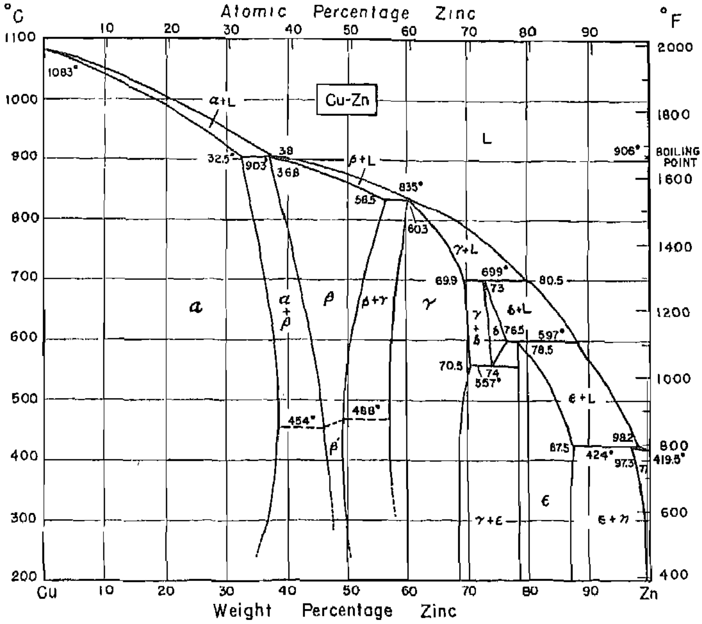

Figure 22-36. Diagram of the copper-zinc system.

Alloys of 37.5 to 38 per cent Zn, which are completely β at near the peritectic temperature and completely α at 450°C and below, can be drastically quenched and undergo the β → α transformation as a diffusion-less or martensitic type reaction. This results in a distorted α structure, face-centered tetragonal.

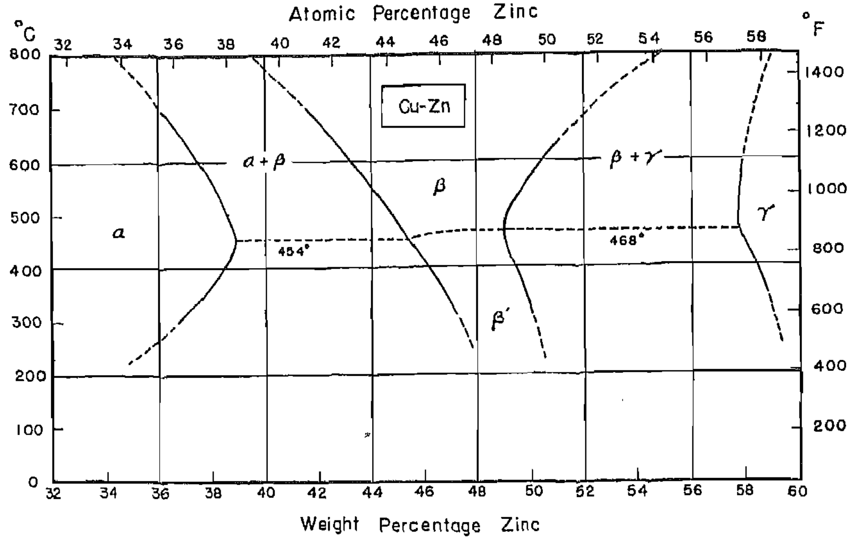

FIGURE 22-37. Enlargement of the copper-zinc diagram between 32 and 60 per cent zinc, below 800°C.

CRYSTAL STRUCTURES OF CU - ZN ALLOYS[6]

Phase	Per Cent Zn	Structure	a (kX)	c (kX)
α	0	F.c.c.	3.608	
α	37.5	F.c.c.	3.693	
β'	48	B.c.c.	2.945	
γ	58.5	Complex cubic	8.837	
γ	67.5	Complex cubic	8.874	
ε	79.0	c.p. hex.	2.762	4.308
η	97.4	c.p. hex.	2.6732	4.8125
η	100	c.p. hex.	2.6590	4.9351

Cu-Zr[6]

The β phase in this system is Cu_3Zr. Age hardening of copper containing about 1 per cent Zr is possible, as might be predicted from the decrease of solubility of Zr in α with decrease in temperature. However, there are yet no industrial applications of this alloy.

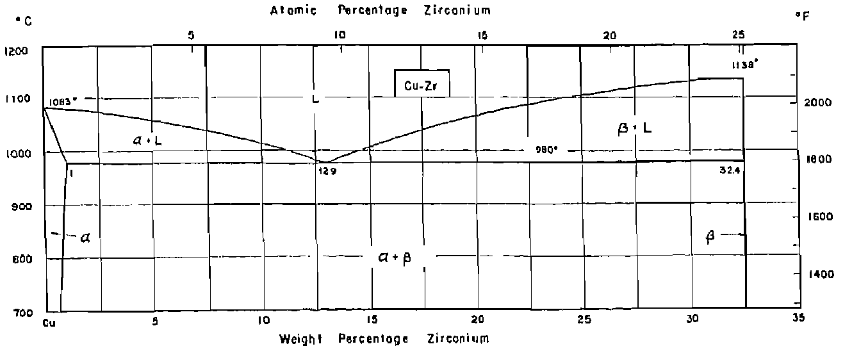

Figure 22-38. Diagram of the copper-zirconium system up to 35 per cent zirconium.

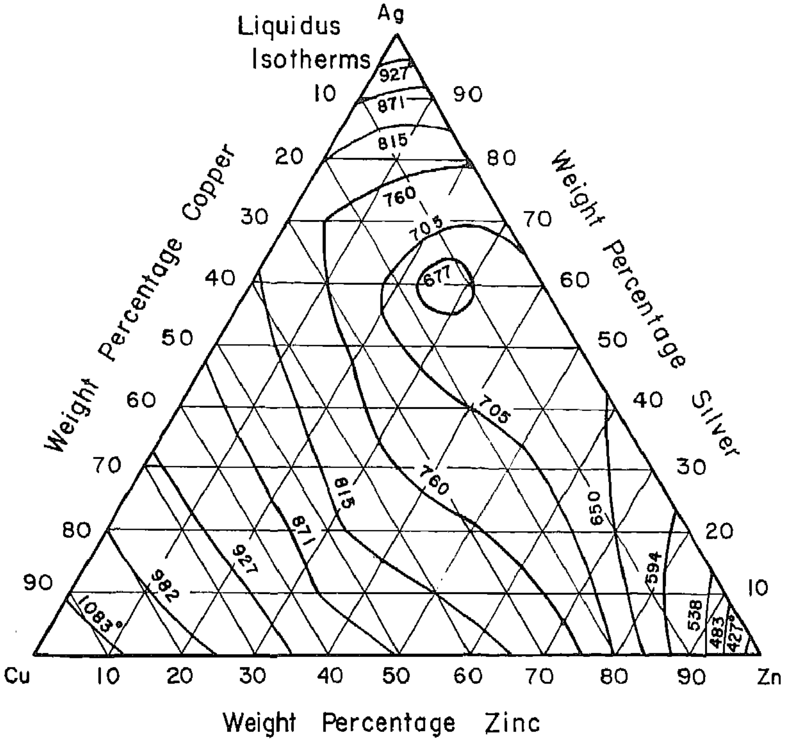

Figure 22-39. Diagram of the copper-silver-zinc system, liquidus isotherms.

PHASE DIAGRAMS OF TERNARY SYSTEMS

Cu-Ag-Zn

The liquidus diagram shown is taken from "The Metals Handbook." The binary Cu-Ag eutectic temperature is depressed with addition of zinc and also the ratio of Cu to Ag in the eutectic is decreased. Up to about 24 per cent zinc, alloys behave as pseudobinary eutectics with zinc in solid solution in the α-silver and α-copper phases of the eutectic.

The binary silver-zinc system is similar to the binary Cu-Zn system with the same type of electron compounds, β (3/2), γ (21/13), and ε (7/4), as well as the terminal solid solutions α and η. There are no ternary compounds, but instead, the β, γ, and ε phases of both systems appear to be isomorphous, so that either copper or silver atoms can replace each other in these electron compounds.

The ternary alloys are of importance in the field of brazing alloys. For this use, cadmium, phosphorus, or tin may be added to make a quaternary alloy. Common alloys in this field are given in Table 22-2.

TABLE 22-2. BRAZING ALLOYS CONTAINING COPPER

Composition					Melting point (°F)	Flow point (°F)
Alloy	Cu	Ag	Zn	Other		
1	52	10	38		1450	1565
2	45	20	35		1430	1500
3	45	20	30	5 Cd	1140	1500
4	30	45	25		1250	1370
5	34	50	16		1240	1425
6	20	65	15		1240	1305
7	20	70	10		1335	1390
8	16	80	4		1330	1490
9*	15.5	50	16.5	18 Cd	1160	1175
10*	80	15		5 P	1190	1300
11	38	30	32		1370	1410
12	36	40	24		1330	1445
13	25	60	15		1260	1325
eutectic	28	72			1435	1435
15*	22	56	17	5 Sn	1165	1200

* Trade names: 9, "Easy Flow"; 10, "Sil Fos"; 15, "Ready Flow."

Cu-Be-Ni

Data are available only for the copper-nickel rich alloys. The addition of small amounts of nickel to Cu-Be alloys raises the temperature of the binary eutectoid reaction at 508°C, $\beta \rightarrow \alpha + \gamma$, as well as changing it from an invariance to univariance. At about 2 per cent Ni, the binary β phase field is obliterated and an invariant reaction is found; $L + \gamma \leftrightharpoons \alpha + \beta$, at 868°C[44]. The reaction goes to the right on cooling. The compositions of the four phases at invariance are:

$L =$ 4.4% Be, 0.8% Ni
$\gamma \sim$ 13.7% Be, 59% Ni
$\alpha =$ 0.8% Be, 1.6% Ni
$\beta =$ 5.7% Be, 2% Ni

Just as Cu and Ni are isomorphous and form a single-phase solid solution, so the γ phase of the Cu-Be system, which represents the compound CuBe, is isomorphous with the equivalent compound NiBe of the nickel-beryllium system. In the ternary diagram, this phase, (CuNi)Be, is the phase in equilibrium with the α solid solution at 500°C. The maximum solubility is at temperatures just below the solidus. The sharp decrease of solubility at low nickel contents corresponds to the disappearance of the β phase of the binary Cu-Be system.

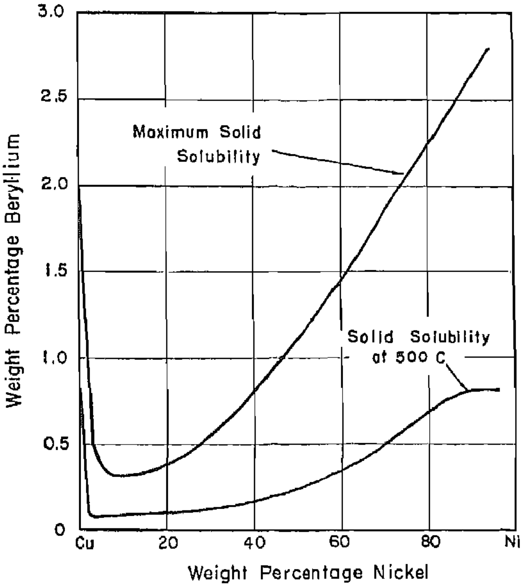

FIGURE 22-40. Solubility of beryllium in copper-nickel solid solutions.

Cu-Ni-Zn[45]

The liquidus surface falls off uniformly from Ni to Cu and from both toward Zn with slight folds, not perceptible in the diagram, for peritectic reactions. The indicated maximum at slightly above 850°C corresponds to congruent solidification of the γ phase on the Ni-Zn side, although the equivalent phase for Cu-Zn alloys forms peritectically.

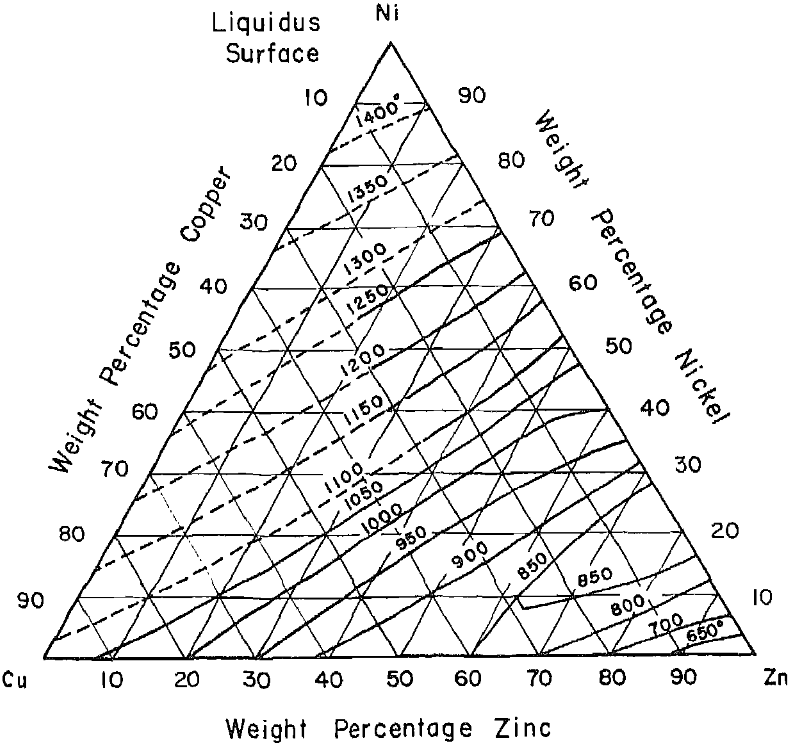

FIGURE 22-41. Diagram of the copper-nickel-zinc system at the liquidus surface.

The ternary isothermal section marked "Low Temperature" represents equilibrium of the system in the vicinity of 300 to 400°C. The body-centered cubic electron compound CuZn or β phase at high temperatures is isomorphous with the equivalent NiZn β phase. When ordering occurs, however, β' of the CuZn system remains cubic, whereas β_1 of the NiZn system becomes body-centered tetragonal and nonisomorphous.

The 21/13 electron compound Cu_5Zn_8, which is a γ phase, complex cubic with 52 atoms per cell, is completely isomorphous with the equivalent γ phase of the NiZn system. The higher nickel content of the NiZn equivalent γ phase results from the effect of nickel supplying no electrons to the electron compound whereas copper supplies one per atom. Hume-Rothery[1] has found many electron compounds of transition metals such as nickel with other elements where the transition metal supplies no electrons and presumably its 4s electrons drop back into unfilled 3d shells.

The 7/4 electron compound $CuZn_3$ or ε with a close-packed hexagonal structure has its counterpart, hexagonal δ, in the Ni-Zn system, but in ternary alloys, the ε and δ are not isomorphous. The zinc-base ternary solid solution, η, has a very limited solution field.

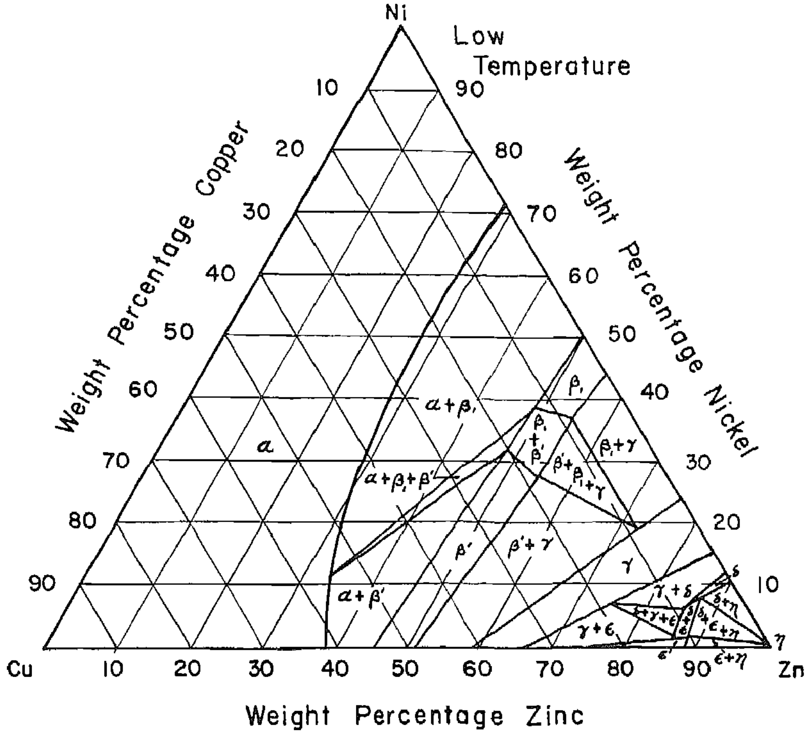

FIGURE 22-42. Diagram of the copper-nickel-zinc system at temperatures below 400°C.

Cu-Sn-Ni

The liquidus surface and the solid solubilities at 300°C for copper-rich alloys are reproduced here from "The Metals Handbook[6, 40]." The ε phase is essentially the binary electron compound Cu_3Sn with an orthorhombic structure. Alloys in the field (α + ε) might show structures of α + δ under usual conditions since the presence of Ni does not probably facilitate the ordinarily sluggish binary eutectoid reaction (δ → α + ε). No information regarding the phase marked θ seems to be available.

Presumably, there is a narrow triangular field of $\alpha + \varepsilon + \theta$ between the $\alpha + \varepsilon$ and $\alpha + \theta$ fields.

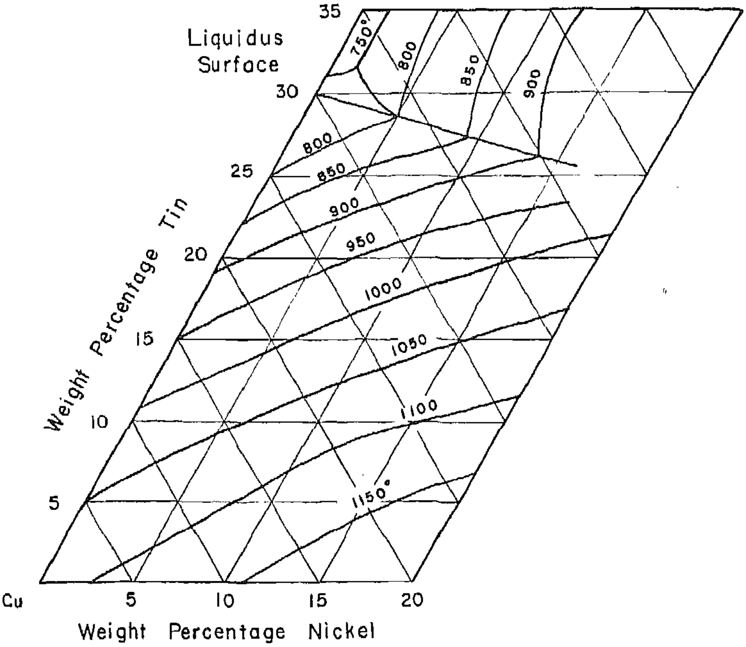

FIGURE 22-43. Liquidus isotherms of the copper-rich alloys of the copper-nickel-tin system.

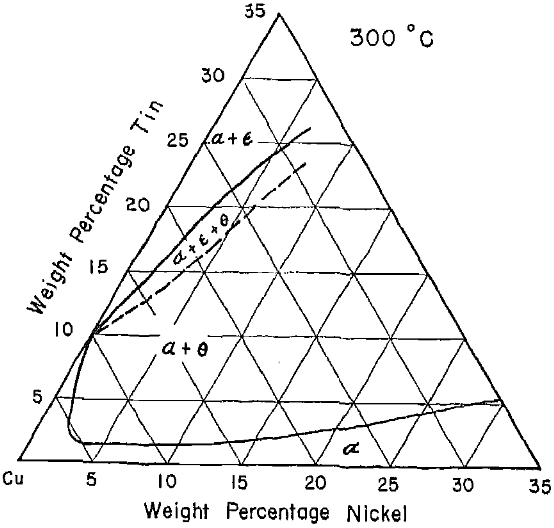

FIGURE 22-44. Isothermal section of the copper-nickel-tin system at 300°C.

Cu-Sn-Zn

The liquidus surface[47] and 500° isothermal sections are presented for copper-rich alloys[47]. In the liquidus diagrams, the designations α and β record the phases forming from the liquid within the indicated compositional field. The heavy line nearest the copper corner represents the peritectic fold and the other represents a change in slope of the liquidus above the γ-phase field.

The β phases of the Cu-Zn and the Cu-Sn systems are isomorphous at high temperatures. The Cu-Sn β phase (or Cu_5Sn) is a 3/2 electron compound which changes to γ and then, in the binary system, eutectoidally decomposes to $\alpha + \delta$ at 520°C. This eutectoid in the ternary system extends nearly to the copper-zinc side, decreasing in temperature with increase in zinc content. Therefore, while the $\alpha + \gamma$ field is correct for most of the diagram, along the Cu-Sn side it should be $\alpha + \delta$. It is for this reason that the line between $(\alpha + \gamma)$ and γ fields of the 500° isothermal section is dashed.

The 500° isothermal section also shows the decrease in solubility of γ in

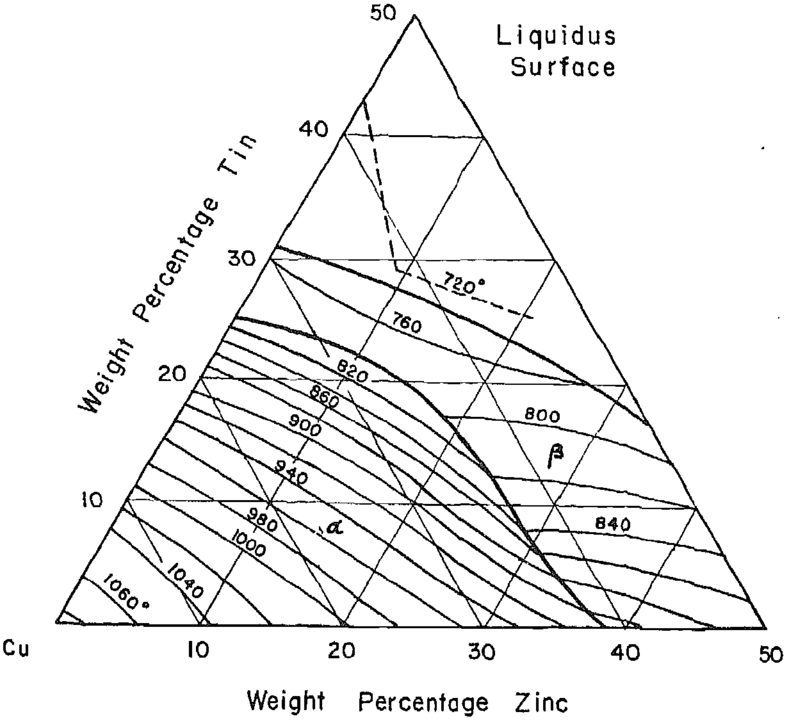

FIGURE 22-45. Liquidus isotherms of the copper-rich alloys of the copper-tin-zinc system.

α with temperature by the changed position of the line separating the α and $(\alpha+\gamma)$ fields at 300°C. The phase in equilibrium with α at 300°C is probably ε rather than γ. The solubility decrease makes possible age hardening of the ternary alloys.

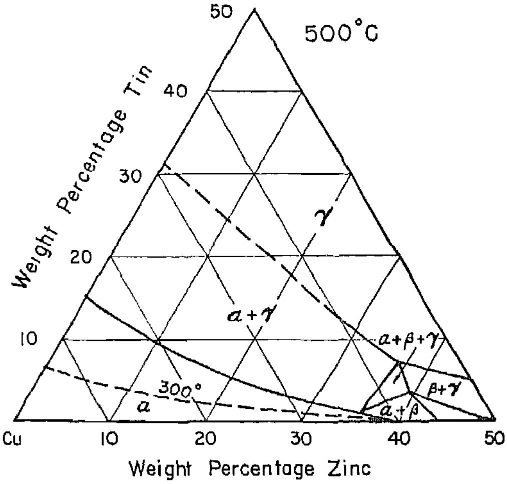

FIGURE 22-46. Diagram of the copper-tin-zinc system at the 500°C isothermal section.

Sn-Cu-Sb

In this system, the tin-rich alloys are the ones of principal engineering use. The liquidus surface of the ternary system is represented by dashed isothermals and heavy solid lines are employed to show critical reactions. These are identified in the accompanying tables with corresponding letters on the diagram.

The complexities of the three binary systems in the solid state are reproduced in the ternary system and it is certain that not all of the phase field boundaries shown here represent final equilibria for solid alloys. Tasaki[48] claims to have identified one ternary compound, $Cu_{12}Sn_7Sb_3$, which appears in the solid alloys at 38.9 per cent Cu, 42.3 per cent Sn, and 18.8 per cent Sb. This phase actually is the η' phase, Cu_6Sn_5, of the binary system, which is labelled here γ' and runs from 39 per cent Cu, 61 per cent Sn over to the composition $Cu_{12}Sn_7Sb_3$. In other words, antimony can replace up to 30 per cent of the tin in the binary Cu-Sn η' phase.

The δ phase shown here at 60 per cent Cu and 40 per cent Sn is the ε phase of the binary Cu-Sn system. The phase labelled here as K is an isomorphous compound going from the γ Cu-Sn phase at 70 per cent Cu, 30 per cent Sn to the δ Cu-Sb phase at 70 to 60 per cent Cu, 30 to 40

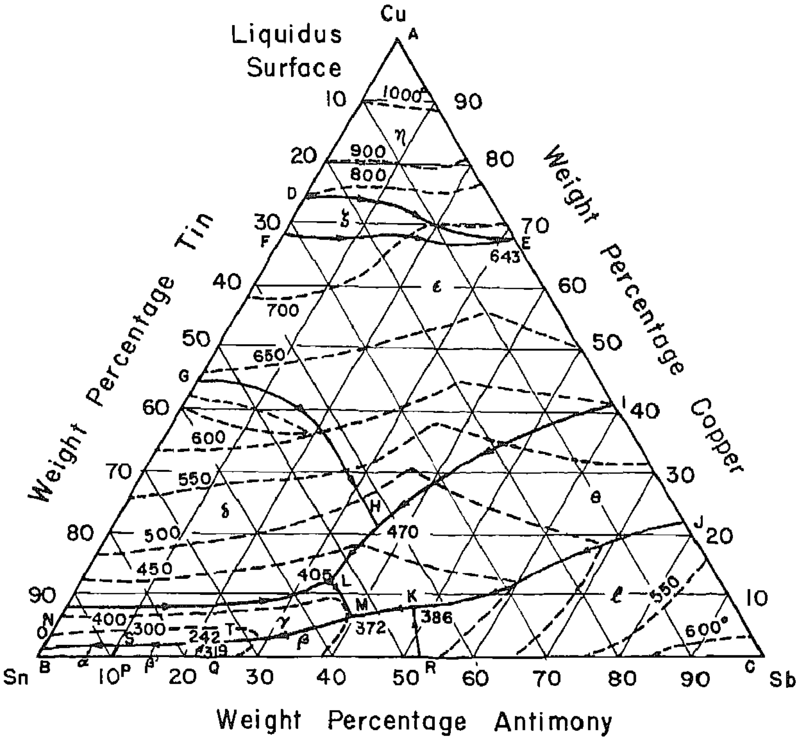

FIGURE 22-47. Diagram of the copper-antimony-tin system at the liquidus surface.

per cent Sb. The phase labelled here as θ at 50 per cent Cu, 50 per cent Sb is Cu_2Sb, called ζ in the binary Cu-Sb system.

It is regrettable that this system is an outstanding example of confusion in labelling, with a particular Greek letter meaning one phase in one binary and a different type of phase in another binary and a still different phase in the ternary system.

PRIMARY CRYSTALLIZATION

Area	Phase forming	Description
OSPB	α	Sn-rich ternary solid solution.
QTMKR	β	Ternary solid solution of Cu in β SnSb.
NLHG	γ	γ or Cu_3Sn of the binary system with some dissolved Sb.
DEF	ζ	Isomorphous ternary solid solution of β Cu-Sb and γ Cu-Sn compounds.
ADE	η	Cu-rich ternary solid solution.
JKRC	ι	Sb-rich ternary solid solution.
IHLMKJ	θ	Cu_2Sb compound.

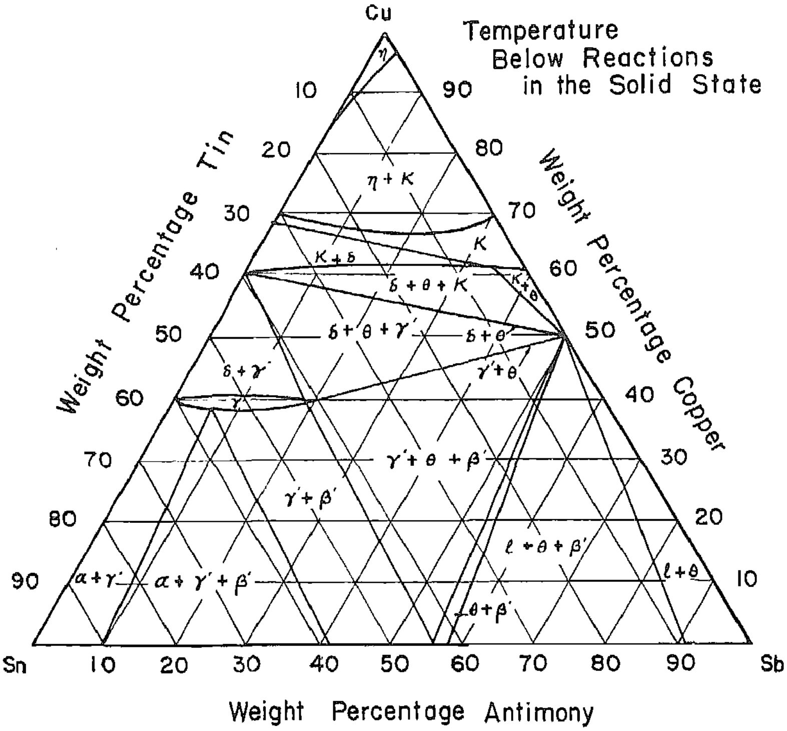

Figure 22-48. Diagram of the copper-antimony-tin system at temperatures below phase changes in the solid state.

Monovariant Equilibria

Reaction Line	Reaction	Type of Reaction
DE	$L + \eta \rightleftharpoons \zeta$	Peritectic
FE	$L + \zeta \rightleftharpoons \varepsilon$	Peritectic
GH	$L + \varepsilon \rightleftharpoons \delta$	Peritectic
HI	$L + \varepsilon \rightleftharpoons \theta$	Peritectic
HL	$L \rightleftharpoons \delta + \theta$	Eutectic
NL	$L + \delta \rightleftharpoons \gamma$	Peritectic
LM	$L + \theta \rightleftharpoons \gamma$	Peritectic
JK	$L \rightleftharpoons \iota + \theta$	Eutectic
KM	$L + \theta \rightleftharpoons \beta$	Peritectic
KR	$L + \iota \rightleftharpoons \beta$	Peritectic
MT	$L \rightleftharpoons \beta + \gamma$	Eutectic
QT	$L + \beta \rightleftharpoons \beta'$	Peritectic
TS	$L \rightleftharpoons \beta' + \gamma$	Eutectic
PS	$L + \beta' \rightleftharpoons \alpha$	Peritectic
OS	$L \rightleftharpoons \alpha + \gamma$	Eutectic

INVARIANT POINTS

Point	Reaction	Type of Reaction	Temperature (°C)
E	$L \rightleftharpoons \eta + \zeta + \varepsilon$	Eutectic	643
H	$L + \varepsilon \rightleftharpoons \delta + \theta$	Peritectic	470
L	$L + \delta \rightleftharpoons \gamma + \theta$	Peritectic	405
K	$L + \iota \rightleftharpoons \beta + \theta$	Peritectic	386
M	$L + \theta \rightleftharpoons \beta + \gamma$	Peritectic	372
T	$L + \beta \rightleftharpoons \gamma + \beta'$	Peritectic	319
S	$L + \beta' \rightleftharpoons \alpha + \gamma$	Peritectic	242

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Chapter 23

Magnetic Properties of Copper and Copper Alloys

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In general terms, copper and most of its alloys are known as non-magnetic materials. More precisely, copper is a diamagnetic substance, having a mass susceptibility (χ) of -0.080×10^{-6} cgs units per gram at ordinary temperatures, equivalent to a gram-atomic susceptibility of -5.1×10^{-6} cgs units. A few copper-base alloys, though containing no ferromagnetic metals, possess strong ferromagnetism, but not to a degree that has made them useful for this property.

The variation of the magnetic susceptibility of copper with temperature is small, as shown by the following data obtained by Honda[7] and Endô[5]:

TABLE 23-1. VARIATION OF THE SUSCEPTIBILITY OF COPPER WITH TEMPERATURE

Temperature (°C)	$\chi \times 10^6$	Temperature (°C)	$\chi \times 10^6$
20	−0.086	900	−0.079
300	− .085	1080 (solid)	− .077
600	− .082	1090 (liquid)	− .054

Copper alloys are the most commonly used materials for construction or housing of instruments in which only weakly magnetic substances can be tolerated because of interference with magnetic devices. Examples of these include compasses, surveying instruments, aircraft instruments, and ordnance aiming circles.

Susceptibility of Alloys

As stated by Endô[5], the susceptibility-concentration curve for binary alloys is a straight line in the case of alloys consisting of a mechanical mixture of the components, and is a curve in the case of solid solutions. When an intermetallic compound is formed, a sharp break occurs in the curve, which may then rise or fall depending on the susceptibility characteristics of the compound.

When sufficiently free from contamination with iron, all of the common brasses and bronzes have very low susceptibilities. Such elements as zinc, lead, tin, aluminum, silicon, and phosphorus added to copper have in themselves only a small effect on its magnetic properties. They may have a greater indirect effect when the alloys contain appreciable amounts of iron as impurity.

Iron added in the amounts used for enhancement of mechanical properties in certain copper alloys causes very large increases in magnetic susceptibility.

Nickel, though ferromagnetic, causes only a small rise in susceptibility which may not be out of line for most applications, up to a point where more than about four-tenths of the copper atoms are replaced by nickel, *i.e.*, until the Ni:Cu ratio exceeds 38:62 weight per cent, at which point the susceptibility is increasing rapidly. This is shown in the data of Kaufmann and Starr[8], given in Table 23-2.

TABLE 23-2. SUSCEPTIBILITIES OF COPPER-NICKEL ALLOYS AT 22°C

Per Cent Nickel	$\chi \times 10^6$	Per Cent Nickel	$\chi \times 10^6$
0	−0.080	20.3	0.55
0.94	− .062	30.0	1.28
5.0	+ .042	35.6	1.99
10.1	.185	38.0	2.84
11.0	.221	50.2	11.8

Manganese is to be avoided in nonmagnetic copper-base alloys, since, although the metal itself is paramagnetic, its structure is close to that which accounts for ferromagnetism[12]; also addition of it is likely to bring iron in with it. The susceptibilities of binary copper-manganese alloys have been determined by Valentiner and Becker[15].

The Effect of Iron as Impurity

The effects of the principal alloying elements in copper-base alloys on their magnetic properties are subsidiary to the effect of iron as impurity. Foundry alloys in particular are likely to have iron introduced as impurity through use of scrap. As long as the percentage of iron is below the solid-solubility limit in the particular alloy, it causes only a small rise in susceptibility. The solubility decreases with decrease in temperature to very small limits, so that iron tends to precipitate on cooling, although the precipitation may be arrested by quenching. The iron may separate from a face-centered cubic lattice, as in copper alloys, without transforming to the body-centered lattice and in this form remain at least partly paramagnetic[1, 14]. It may subsequently become ferromagnetic through slight plastic deformation, and a large rise in susceptibility then occurs.

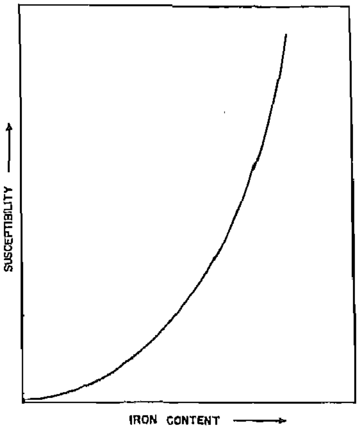

Figure 23-1. Typical graph of the effect of small amounts of iron on the susceptibility of copper-base alloys.

These changes, without plastic deformation, result in variation of susceptibility with iron content somewhat in accordance with the curve shown in Figure 23-1, which is typical of the effect of iron as impurity in the common copper-base alloys. A slow rise with increasing iron in small percentages gives way to a more rapid transitional increase, followed by a steep rise at higher iron contents.

Single-phase alloys appear to have the best behavior as regards permissible iron content, at least when the formation of a second phase promotes the precipitation of iron. The appearance of the beta phase in brass causes a marked rise in magnetic properties[14].

Susceptibilities of Copper-Base Alloys

Table 23-3 gives the mass susceptibilities of a number of the common copper-base alloys, including both casting and wrought alloys. These are given for a normally negligible iron content (0.01 per cent), and for 0.15 per cent iron, the latter illustrating the effect of a small iron content which is nevertheless below the maximum limit given in standard specifications (based on their usual applications) for all the casting alloys and most of the wrought alloys.

The values given in Table 23-3 were determined by Butts and Reiber[3], who studied the susceptibilities and residual magnetic moments of 19 copper-base alloys, with particular reference to the effect of small amounts of iron. The magnetic properties were measured for varying percentages of iron and under different conditions of thermal and mechanical treatment. Sixteen of the alloys were judged suitable for magnetic instrument construction if the iron content were as low as 0.01 per cent.

Table 23-3. Susceptibilities ($\chi \times 10^6$) of Copper-base Alloys

Alloy No.	Nominal Composition, Per Cent Cu-Sn-Pb-Zn	Casting Alloys			
		0.01 Per Cent Fe		0.15 Per Cent Fe	
		As Cast	After Solution-Quench Treatment	As Cast	After Solution-Quench Treatment
4 A	85-5-5-5	0.1	0.1	0.9	0.1
5 A	81-3-7-9	0.1	0.1	1.3	0.4
6 B	67-1-3-29	....	....	0.9	0.2
2 B	87-8-1-4	....	....	4.5	0.4
2 A	88-6-1.5-4.5	....	....	6.3	0.8
1 B	88-8-4	....	....	3.4	1.1
6 A	71-1-3-25	0.1	0.1	16	6.0
B 22 A	80.5-19 Sn-0.5 P	0.1	−0.1	67	8.5
		Wrought Alloys			
		0.01 Per Cent Fe		0.15 Per Cent Fe	
		As Rolled	After Solution-Quench Treatment	As Rolled	After Solution-Quench Treatment
B 169 C	92 Cu-8 Al	−0.2	−0.1	1.3	0.1
B 151 C	62 Cu-19 Zn-18 Ni-1 Pb	+0.4	+0.5	0.8	0.7
B 16	60-3-37	0.1	0.0	2.6	3.8
B 152 A	Electrolytic Cu	−0.1	−0.1	6.1	0.1
B 139 A	95 Cu-5 Sn +P	0.0	0.0	17	43
B 21 A	62-0.5-36.5	0.1	−0.1	42	1.7
B 36 8	67 Cu-33 Zn	0.1	−0.1	58	1.0

Among the casting alloys tested, 85-5-5-5 (4 A), valve composition (5 A), and commercial yellow brass (6 B) permitted iron contents up to 0.15 per cent without serious increase in magnetism. Among the wrought alloys, binary aluminum bronze (B 169 C) was rated the best alloy at low iron contents (up to 0.15 per cent Fe), and 18 per cent nickel silver (B 151 C) at higher iron contents, *e.g.*, up to 0.4 per cent Fe. Nickel is effective in counteracting the presence of small amounts of iron in alpha brasses (though not in tin-bearing bronzes), since it causes iron to be retained in solid solution in the ternary Cu-Ni-Fe system, in which mode of occurrence iron has relatively little effect on magnetism.

The magnetic properties of all the alloys tested are lowered, as shown in Table 23-3, by giving them a solution heat treatment followed by quenching. In many cases, however, such a treatment would not be feasible in practice because it results in excessive grain growth which renders the alloys unfit for use because of deterioration of their mechanical properties. If the iron is caused to precipitate from solution either by annealing with slow cooling or by cold working, the magnetic properties are also greatly increased, the effect increasing with rise of iron content.

The magnetic properties were not found to increase appreciably through prolonged aging at temperatures up to 100°C, except when the iron content was so high as to render the alloy initially unfit for purposes requiring low magnetic properties.

Effect of Iron Added to Pure Copper

Small amounts of iron present in otherwise pure copper causes a steeper rise than in the case of the common copper alloys. The effect is given in Figure 23-2 as determined by Bitter and Kaufmann[1] and by Butts

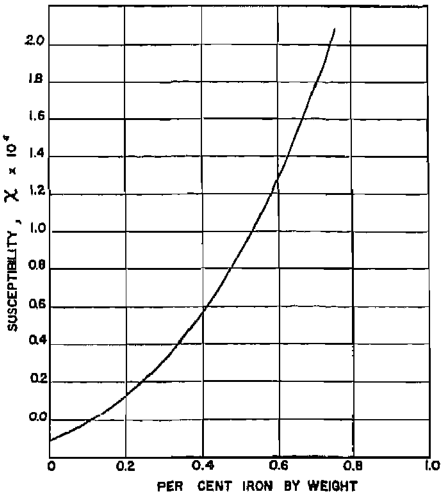

FIGURE 23-2. The effect of iron on the susceptibility of copper heated at 950°C (1740°F) and quenched in water.

and Reiber. The values plotted are for rolled specimens heated 12 hours or more at 950°C (1740°F) and then quenched in water. Rolled specimens not thus heat treated gave considerably higher values, but if the iron content is as low as 0.01 per cent, electrolytic copper is suitable for magnetic instrument construction.

MAGNETIC COPPER-BASE ALLOYS

There are numerous instances of nonferrous alloys containing no ferromagnetic components but exhibiting varying degrees of ferromagnetism. The best known of these are the Heusler alloys, which have been studied by several investigators. The original discovery by Heusler in 1898 embraced a series of Cu-Mn-Al alloys, the most magnetic of which have saturation magnetizations of the same order as nickel. The highest saturations are found in the Cu-Mn-Al series. The Heusler alloy containing 75 Cu, 15 Mn, 10 Al has a maximum permeability of 100 to 1,000, saturation induction of 6,000 gausses, and saturation hysteresis of 300 to 450 ergs per cubic centimeter. The coercive force varies from 1 to 200 oersteds[2]. These values were obtained by Take on specimens quenched from 600°C (1110°F) and aged at 209°C (408°F). The highest saturation magnetizations in the above two series are found close to the compositions Cu_2MnAl and Cu_2MnSn[2, 6].

Besides Cu-Mn or Mn alone, Heusler alloys may contain *instead of* Al or Sn *one* of the elements As, Sb, Bi, or B. Alloy compositions approximating Cu_2MnIn and Cu_2MnGa also are ferromagnetic.

The Heusler alloys can be worked mechanically when the manganese content is under 24 per cent. The highest Curie point found is about 450°C (840°F), but in most of the alloys it is about 330°C (625°F).

Although the Heusler alloys have copper as the largest component, the cause of ferromagnetism in them is associated with the compositional presence of manganese. It has been shown by Slater[13] that ferromagnetism is likely to occur when manganese atoms are arranged in a space lattice with a certain interatomic distance, and that their separation in the Heusler alloys has this spacing, whereas in pure manganese the separation is too small. It does not permit an amount of electron spin alignment that will result in ferromagnetism. The necessary structural arrangement and spacing occur in the above two systems only within certain phase boundaries.

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Chapter 24

Copper-Base Foundry Alloys

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Early in the art the worker in copper alloys realized that a difference existed in the character of metal used for casting as compared to that which would be hot or cold worked. In general, foundry alloys differ from wrought alloys in the following respects:

(1) They are not easily workable.

(2) The alloying metals, such as lead, tin, iron, aluminum, etc., are generally greater in amount than in wrought alloys, and are a necessary part of the composition.

(3) Elements present as impurities are greater in amount than in wrought metals, but are not considered harmful within the limits of the specifications.

(4) Cast alloys are generally made into intricate shapes, requiring cores, or are of such irregular shapes as to be impractical to roll, forge, or stamp from wrought material.

Up to about 1915, the greater part of the copper-base foundry alloys were made from virgin or primary metals. Industry had not generally accepted the use of composition ingot and considerable prejudice existed against ingot made from secondary metals.

The technical advances made by leading ingot brass and bronze producers during the last decade have been particularly impressive. Operations have been made more efficient and the refining processes have been placed under laboratory control. Only with accurate control has it been possible for manufacturers to demonstrate consistency in delivering ingot metal to meet chemical specifications and physical properties.

Specialization has created a demand for many alloys of unusual composition with specific properties. One of these alloys may comprise an entire casting, or many such alloys may be used in a complete assembly. For example, a valve may have a silicon bronze body, a manganese bronze or silicon bronze stem, a high nickel-silicon or a high nickel-aluminum seat and disk, and an iron handle.

Only a competent ingot manufacturer can produce quality ingot from complex raw material. Certainly the foundry, even though it has strictly modern equipment and may produce castings of the very best quality, is completely lacking in essential facilities to substitute the complex assortment of industrial scrap for quality ingot. It is both uneconomical and hazardous for the foundry to use scrap, because it is not enough simply to sort and grade the raw material and later select certain grades to remelt. On the contrary, the production of ingot metal requires scientifically controlled smelting and refining processes and supervision of trained metallurgists.

These refining and alloy adjusting processes are not commercially feasible in small furnaces, but require large furnaces handling large quantities of metal. The usual practice is to melt a large tonnage at one time, refine the heat by the use of proper fluxes and slag-forming materials and correct metallurgical and furnace practice, analyze the heat while in the molten state, make the necessary metal additions to adjust to the desired composition, deoxidize the heat as may be necessary, and then cast the metal into ingot. Sample ingots, periodically set aside during the casting cycle, are drilled to obtain a final chemical analysis. The entire cycle is supplemented with furnace log data, physical and mechanical tests, and metallographic examination. A high-quality product is thus assured.

An excellent comparison of the use of ingot metal as compared with virgin metal for copper alloy castings is found in a paper by Wolf[2]. He gives data on percentage losses experienced by a large manufacturer who ran a comparison campaign over a four-month period on ingot and virgin metal. Approximately 400,000 pounds of each kind of metal was used and poured in about 175,000 castings. The results obtained are summarized as follows:

(1) Metal cost of ingot was considerably less than that of virgin metal at the time this test was conducted.

(2) The use of ingot showed a saving in storage room, in time consumed in making up charges, in preparation of metals for weighing, and in alloying time.

(3) Regardless of the furnace used in melting, fractures of test plugs made from ingot metal were superior to those made from virgin metal.

(4) Melting loss was about the same on ingot as on virgin metal.

(5) Foundry and test-bench losses were lower on castings from ingot than on those from virgin metal.

(6) Ingot easily met A.S.T.M. specification requirements for tensile strength and elongation.

(7) After chemical treatment, castings from ingot metal had a slight advantage over virgin metal as to appearance.

(8) There was no evidence that the advantages obtained by using ingot metal in preference to virgin metal were offset by any disadvantages.

Nomenclature of Brass and Bronze Alloys

There has been considerable confusion in the use of the terms "brass" and "bronze." Alloys that are of almost identical composition have often been referred to by different names. Nomenclature is discussed in the National Bureau of Standards' Letter Circular 487 (1937), portions of which are quoted below:

> The first bronze was essentially an alloy of copper with tin, whereas brass was an alloy of copper with zinc, but it was soon found that the addition of other metals to the simple binary copper-tin alloy often resulted in a material with improved properties, such as strength and corrosion resistance or more pleasing appearance. Consequently, many of our nominal copper-tin alloys contain both tin and zinc and sometimes other metals. In such alloys it is often difficult to determine whether the zinc or the tin has a predominating effect; the decision cannot be based on the numerical percentages of the two since a given amount of tin usually has more effect than an equal percentage of zinc. With increasing complexity in the composition of the alloys, it becomes increasingly difficult to determine whether a given alloy should be called a brass or a bronze. In those cases where a distinction between brass and bronze could be made, there has been no great misuse of the term "brass," save that in railroad engineering parlance any kind of a bearing is often called a "brass," referring to the bearing rather than to the alloy of which it is made. On the other hand, misapplications of the term "bronze" are frequently encountered. Bronze has long been generally accepted as being superior in a number of ways to brass and advantages of this fact were taken in applying the term "bronze" to newly developed alloys. The term "bronze" has been applied to so many copper alloys that the simple alloys of copper with tin are now often referred to as "tin bronze."
>
> Brass is an alloy consisting essentially of copper (50 to 95 per cent) and zinc (50 to 5 per cent). If the zinc content is greater than 30 per cent the alloy is a "high brass" or a "yellow brass," whereas if the zinc content is less than 20 per cent the alloy is a "low brass." Brass containing an intentional admixture of lead for improving its machining characteristics is known as "leaded brass" or "lead brass." Alloys that contain more than 50 per cent zinc are usually designated as "zinc-base alloys."
>
> Brass of the general composition 60 per cent copper, 40 per cent zinc is widely

known as "Muntz metal," but such names for specific compositions are less commonly applied to brasses than to bronzes. However, some specific terms may be very misleading. For example, the name "German silver" or "nickel silver" refers to the white color of the alloys, not to their composition.

Examples of the improper application of the term "bronze" are found in the alloys known as "architectural bronze," "manganese bronze," and "bronze" screen wire cloth.

An illustration of confusion in nomenclature is encountered in the widely used alloy containing 85 per cent copper, 5 tin, 5 zinc, and 5 lead. This alloy is as frequently called "valve bronze" as it is "red brass;" it is also known as "ounce metal" because the constituents are in the ratio of 1 ounce of each to about 1 pound of copper. On the basis of structure, there is good reason for calling this alloy a bronze and it appears in the list of bronzes covered by Federal Specifications QQ-B-691, for casting bronzes. Another alloy in this same list of bronzes, however, contains 80 per cent copper, 13 zinc, and 4.5 tin. Numerous other examples of nonuniformity and inconsistency in naming alloys of this general type in specifications might easily be cited.

Alloys containing from 10 to about 30 per cent lead, regardless of any zinc present, are known as "leaded bronze" and are widely used in bearings. The name "zinc bronze" has been used to some extent for copper-tin alloys modified by the admixture of zinc, but for brevity the word "zinc" is often omitted and the material referred to simply as "bronze." Two widely used alloys in this class are the "88-10-2" alloy (88 per cent copper, 10 tin, and 2 zinc) and its modern counterpart, the "88-8-4" alloy.

Phosphor Bronze. According to current commercial usage, phosphor bronze may be any composition known as bronze in which the phosphorus content is not less than 0.05 per cent and may be as great as 2 per cent. An alloy of any composition which has simply been deoxidized with phosphorus after melting, and which may contain up to 0.01 or 0.02 per cent phosphorus, is not considered a phosphor bronze.

Government Bronze. There is a widespread but erroneous belief that there is a definite composition officially accepted by the Federal Government as the "best" bronze. One of the alloys of longest commercial use is the 88-10-2 alloy. In the days when cannon were made of bronze this was known as "gun bronze," and for many years this alloy appeared as "Composition G" in the United States Navy specifications. It also appeared in specification B10-18 of the American Society for Testing Materials, but this specification is now replaced by B60-36 for the 88-8-4 alloy. Although this composition is, on the whole, a better all-around alloy for many purposes than 88-10-2, it is not to be designated a "government bronze" any more than any of the others covered by Federal specifications.

In the field of "statuary bronzes" or "art bronzes," there is a similar erroneous idea that there is a preferred "government bronze." Noted statues vary so in composition that it is clear that there are no fixed ideal proportions for art bronze, as well as no U.S. Government standard.

Examples of the tendency to apply the name bronze to copper alloys other than those containing tin are found in "aluminum bronze," "silicon bronze," and "conductivity bronze."

Aluminum Bronze. The term "aluminum bronze" is used commercially to designate copper-base casting alloys with an aluminum content in excess of 7 per cent. Elements such as tin, nickel, manganese, iron, and others may be also present.

Silicon Bronze. This name is often applied to a class of high-strength copper alloys which have recently received much attention. The name "copper-silicon alloy" is used in Federal specifications and suggests silicon as the essential alloying constituent. However, other alloying elements such as manganese, zinc, iron, and tin are often present and the percentage of some of these may equal the silicon content. These alloys are outstanding in many respects and their commercial use, particularly in wrought forms, is increasing.

The term bronze is widely used as descriptive of the surface appearance of metals, especially with reference to the decorative effect. The designation of a leaded brass as "architectural bronze" is justified only on this basis. Certain decorative surface effects are described as "bronzed;" such a one is that given to steel by copper plating it and then treating it with a sulfide solution. Another use is in reference to the metallic pigments used in "bronzing paints." Finely divided metal in the form of flaky particles, whether copper, copper-zinc alloy, or aluminum, is termed "bronze."

CLASSIFICATION OF CAST COPPER-BASE ALLOYS

The classification given in Table 24-1 is based upon the inclusion in the term "copper" all alloys containing 98 per cent or more of copper; upon the inclusion in the term "brass" all copper-base alloys containing an appreciable amount of zinc; and upon the inclusion in the term "bronze" all copper-base alloys containing alloying elements other than zinc in sufficient amounts to be predominant over the effect of zinc in the alloy[1].

TABLE 24-1. CLASSIFICATION OF CAST COPPER-BASE ALLOYS

Class	Addition Elements	Remarks
Copper	Not over 2% total of arsenic, zinc, cadmium, silicon, chromium, silver, or other elements	Conductivity copper castings, pure copper, deoxidized copper, and slightly alloyed copper
Brasses		
Red brass	2-8% zinc. Tin less than zinc. Lead less than 0.5%	Alloys in this class without lead seldom used in foundry work
Leaded red brass	2-8% zinc. Tin less than 6%, usually less than zinc. Lead over 0.5%	Commonly used foundry alloys. May be further modified by addition of nickel
Semi-red brass	8-17% zinc. Tin less than 6%. Lead less than 0.5%	Alloys in this class without lead seldom used in foundry work

TABLE 24-1. CLASSIFICATION OF CAST COPPER-BASE ALLOYS (*Continued*)

Class	Addition Elements	Remarks
Leaded semi-red brass	8-17% zinc. Tin less than 6%. Lead over 0.5%	Commonly used foundry alloys. May be further modified by addition of nickel
Yellow brass	Over 17% zinc. Tin less than 6%. Under 2% total aluminum, manganese, nickel, iron, or silicon. Lead less than 0.5%	Commonly used foundry alloy
Leaded yellow brass	Over 17% zinc. Tin less than 6%. Under 2% total aluminum, manganese, nickel, or iron. Lead over 0.5%	Commonly used foundry alloy
High-tensile yellow brass	Over 17% zinc. Over 2% total of aluminum, manganese, tin, nickel, and iron. Silicon under 0.5%. Lead under 0.5%. Tin less than 6%	Commonly used foundry alloys under name of "manganese bronze" and various trade names
Leaded high-tensile yellow brass	Over 17% zinc. Over 2% total of aluminum, manganese, tin, nickel, and iron. Lead over 0.5%. Tin less than 6%	Commonly used foundry alloys
Silicon brass	Over 0.5% silicon. Over 3% zinc	Commonly used foundry alloys
Tin brass	Over 6% tin. Zinc more than tin	Alloys in this class seldom used in foundry work
Tin-nickel brass	Over 6% tin. Over 4% nickel. Zinc more than tin	Alloys in this class seldom used in foundry work
Nickel brass (nickel silver)	Over 10% zinc. Nickel in amounts sufficient to give white color. Lead under 0.5%	Commonly used foundry alloys sometimes called "German silver"
Leaded nickel brass (leaded nickel silver)	Over 10% zinc. Nickel in amounts sufficient to give white color. Lead over 0.5%	Commonly used foundry alloys sometimes called "German silver"
Bronzes		
Tin bronze	2-20% tin. Zinc less than tin. Lead less than 0.5%	Commonly used foundry alloys. May be further modified by addition of some nickel or phosphorus, or both
Leaded tin bronze	Up to 20% tin. Zinc less than tin. Lead over 0.5%, under 6%	Commonly used foundry alloys. May be further modified by addition of some nickel or phosphorus, or both
High-leaded tin bronze	Up to 20% tin. Zinc less than tin. Lead over 6%	Commonly used foundry alloys. May be further modified by addition of some nickel or phosphorus, or both
Lead bronze	Lead over 30%. Zinc less than tin. Tin under 10%	Used for special bearing applications
Nickel bronze	Over 10% nickel. Zinc less than nickel. Under 10% tin. Under 0.5% lead	Commonly used foundry alloys. Sometimes called "German silver" or "nickel silver"
Leaded nickel bronze	Over 10% nickel. Zinc less than nickel. Under 10% tin. Over 0.5% lead	Commonly used foundry alloys. Sometimes called "German silver" or "nickel silver"

TABLE 24-1. CLASSIFICATION OF CAST COPPER-BASE ALLOYS (*Continued*)

Class	Addition Elements	Remarks
Bronzes		
Aluminum bronze	5 to 15% aluminum. Up to 10% iron, with or without manganese or nickel. Less than 0.5% silicon	Commonly used foundry alloys. Some may be heat treated. May be further modified by addition of tin
Silicon bronze	Over 0.5% silicon. Not over 3% zinc. Not over 98% copper	Commonly used foundry alloys. Some are readily heat treated
Beryllium bronze	Over 2% beryllium or beryllium plus metals other than copper	Most of these alloys are heat treatable

BBII STANDARD ALLOYS[1]

In 1929 over 600 copper-base alloys were in use in the foundry industry, in addition to many special compositions usually classified as high-strength alloys. Over 40 specifications existed for the alloy of the nominal composition 85 per cent copper, 5 tin, 5 lead, and 5 zinc, commonly called 85-5-5-5.

In 1931, specifications were set up to include only 20 alloys, grouped into five general classes, namely, bronze, red brass, semi-red brass, yellow brass, and high-lead alloys. Tables appended to the chemical specifications contained data on approximate mechanical properties, examples of use, foundry manipulation, and machining characteristics. Minor revisions were made at intervals in these specifications. The title of the standards now is "Tentative Standard Specifications for Copper-base Alloys in Ingot Form for Sand Casting," and the designation is ASTM B30-45T, revised January 1, 1951, B30-49.

During 1939, the Brass and Bronze Ingot Institute in a resurvey found that over 100 brass and bronze ingot metal alloys were still in use, but that 23 alloys represented over 80 per cent of the tonnage produced. Current usage was appraised and the alloys corresponding thereto were determined. Specification limits were then set for the major elements and for impurities. These had to be set so as to assure the user a uniform and high-quality product, but at the same time to conform to practical limits for the production of the alloys in ingot form.

Detailed composition limits for each alloy as later revised are shown in the following pages. The alloys have been classified in accordance with the tentatively approved classification system and have been given number designations instead of serial numbers. The Brass and Bronze Ingot Institute recommends the adoption of these number designations by all users, producers, technical societies, and writers.

Physical Properties of BBII Ingot Brass and Bronze Alloys

The physical properties of castings of the brasses and bronzes are the combined result of the composition of the alloy, the cleanliness of the metal, and the processing steps for the casting to be tested. The properties may vary somewhat as the percentages of the major constituents are at or near the minimum or maximum limits permitted in the specifications for the alloy. They may vary to a lesser degree as the result of other elements present, even though the amounts are within the limits permitted in the specification.

Strength, ductility, hardness, etc. of castings are all subject to variation due to grain size. In general, the coarser the grain, the lower will be the tensile strength, elongation, reduction in area, hardness, and impact strength. Grain size is dependent chiefly upon the rate of cooling of the casting, which is influenced by many variables.

Test bars cut from chill-cast ingot or chill-cast coupons may have different physical properties from those cut from sand castings. Test bars cast to size in sand will have different physical properties from those cut from sand-cast coupons or blocks or cut from a finished casting.

It is obvious, then, that no specific physical properties can be stated as representative of each of the standard alloys, but it is possible to set down ranges for physical properties. These are shown in the following tables. These properties are dependent on foundry technique, proper melting, pouring, gating, venting, and feeding.

Complete data for modulus of elasticity, compression strength, impact strength, coefficients of expansion, thermal and electrical conductivity, specific heat, melting point, etc. are not available on all of the alloys.

With proper foundry practice, castings made from high-quality brass and bronze ingot metal will show physical properties within the ranges indicated.

LEADED TIN BRONZE
A.S.T.M. B30-51 Alloy 2A
Nominal Composition: 88-6-1½-4½

*Chemical Analysis, per cent**

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P
Minimum	86.00	5.75	1.25	3.50							
Nominal	88.00	6.00	1.50	4.50							
Maximum	89.00	6.50	1.75	5.00	0.75[a]	0.20	0.25	0.05	none[b]	0.005	0.03

Physical Properties

Tensile strength, psi	36,000 — 48,000
Yield strength, psi	16,000 — 21,000
Elongation, per cent in 2 inches	25 — 40

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* For footnotes, see page 533.

LEADED TIN BRONZE Nominal Composition: 88-6-1½-4½ (*Continued*)

Reduction of area, per cent	16 — 33
Modulus of elasticity, psi × 10^6	12 — 16
Brinell hardness (10-mm ball, 500-kg load)	60 — 72
Compression strength, psi:	
0.001 inch set	12,000 — 15,000
0.1 inch set	30,000 — 38,000
Impact strength (Izod), ft-lb	11 — 16
Specific gravity	8.60 — 8.80
Weight per cu inch, pounds	0.311 — 0.318
Patternmakers' shrinkage, inch per foot	3/16 — 7/32
Electrical conductivity, per cent I.A.C.S.	13 — 15
Coefficient of thermal expansion	0.0000103
Melting point	1800 — 1830°F
Pouring temperature, light castings	2000 — 2300°F
Pouring temperature, heavy castings	1900 — 2150°F

Uses

- Known as steam or valve bronze
- High-grade steam metal or valve bronze involving temperatures up to 550°F
- Steam-pressure castings
- Backing for babbitt-lined bearings
- Carburetors
- Automobile brackets
- Oil pumps
- Gears
- Electrical castings
- Bushings
- High-duty bearings
- Ornamental bronze

LEADED TIN BRONZE
A.S.T.M. B30-51 Alloy 2C
Nominal Composition: 87-10-1-2

*Chemical Analysis, per cent**

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P
Minimum	86.00	9.25	0.80	1.25							
Nominal	87.00	10.00	1.00	2.00							
Maximum	88.50	10.50	1.25	2.50	0.75[a]	0.15	0.25	0.05	none[b]	0.005	0.03

Physical Properties

Tensile strength, psi	36,000 — 46,000
Yield strength, psi	18,000 — 26,000
Elongation, per cent in 2 inches	15 — 25
Reduction of area, per cent	12 — 26
Modulus of elasticity, psi × 10^6	10.6 — 16
Brinell hardness (10-mm ball, 500-kg load)	65 — 80
Compression strength, psi:	
0.001 inch set	12,000 — 14,000
0.1 inch set	40,000 — 46,000
Impact strength (Izod), ft-lb	7 — 10
Specific gravity	8.70 — 8.87
Weight per cu inch, pounds	0.314 — 0.320
Patternmakers' shrinkage, inch per foot	3/16 — 7/32
Electrical conductivity, per cent I.A.C.S.	10 — 12
Thermal conductivity, per cent of Cu	12 — 13

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* For footnotes, see page 533.

LEADED TIN BRONZE Nominal Composition: 87-10-1-2 (*Continued*)

Coefficient of thermal expansion (70—350°F)	0.000010
Melting point	1800 — 1830°F
Solidification range	1830 — 1570°F
Pouring temperature, light castings	2100 — 2300°F
Pouring temperature, heavy castings	1920 — 2100°F

Uses

- Commercial bronze for high-duty bearings where wear resistance is essential
- Strong general utility structural bronze for use under severe conditions
- Bolts, nuts, gears
- Heavy-pressure bearings and bushings to use against hardened steel
- Valves, expansion joints, special high-pressure pipe fittings
- Pump pistons
- Bearings, elevator and electrical work
- Steam-pressure castings
- High-pressure valves
- Automobile bushings

HIGH-LEADED TIN BRONZE
A.S.T.M. B30-51 Alloy 3A
Nominal Composition: 80-10-10

*Chemical Analysis, per cent**

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P
Minimum	78.00[c]	9.25	9.00								
Nominal	80.00	10.00	10.00								
Maximum	81.00	10.50	10.75	0.75	0.75[c]	0.10	0.50	0.08	none[b]	0.003	0.03

Copper plus tin plus lead plus nickel must total a minimum of 98.50 per cent.

Physical Properties

Tensile strength, psi	27,000 — 37,000
Yield strength, psi	15,000 — 22,000
Elongation, per cent in 2 inches	8 — 12
Reduction of area, per cent	5 — 11
Modulus of elasticity, psi × 10^6	8.5 — 13
Brinell hardness (10-mm ball, 500-kg load)	55 — 70
Compression strength, psi:	
0.001 inch set	12,500 — 16,000
0.1 inch set	40,000 — 47,000
Impact strength (Izod), ft-lb	2 — 8
Specific gravity	8.9 — 9.1
Weight per cu inch, pounds	0.321 — 0.329
Patternmakers' shrinkage, inch per foot	1/8 — 3/16
Thermal conductivity, per cent of Cu	12
Coefficient of thermal expansion (70—400°F)	0.0000102
Melting point	1760 — 1770°F
Pouring temperature, light castings	2000 — 2250°F
Pouring temperature, heavy castings	1850 — 2100°F

Uses

- Standard general-purpose bushing or bearing alloy
- Bearing metal; good antifriction and wearing properties for high-speed and heavy-pressures bearing service
- Bearings for heavy pressure, not machined by broaching

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* For footnotes, see page 533.

HIGH-LEADED TIN BRONZE Nominal Composition: 80-10-10 (*Continued*)

Cast bearings and bushings and castings to resist some of the mild acids such as are found in mine waters
Acid-resisting bronze for paper-mill sulfite liquor
Excellent wearing material under conditions of high speed, heavy pressure, shock, and vibration
Used for most types of machine bearings
Roll-neck bearings
Lathe bearings
Babbitt-lined armature bearings for electric locomotives

HIGH-LEADED TIN BRONZE
A.S.T.M. B30-51 Alloy 3B
Nominal Composition: 83-7-7-3

*Chemical Analysis, per cent**

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P
Minimum	82.00[c]	6.50	6.50	2.50							
Nominal	83.00	7.00	7.00	3.00							
Maximum	84.00	7.50	7.75	4.00	0.50[c]	0.15	0.25	0.08	none[b]	0.003	0.03

Physical Properties

Tensile strength, psi	30,000 — 38,000
Yield strength, psi	17,000 — 21,000
Elongation, per cent in 2 inches	12 — 20
Reduction of area, per cent	10 — 22
Modulus of elasticity, psi $\times 10^6$	14 — 16.8
Brinell hardness (10-mm ball, 500-kg load)	55 — 65
Specific gravity	8.85 — 8.90
Weight per cu inch, pounds	0.320 — 0.322
Patternmakers' shrinkage, inch per foot	3/16 — 7/32
Coefficient of thermal expansion (30—200°F)	0.000010
Melting point	1750 — 1800°F
Pouring temperature, light castings	2000 — 2250°F
Pouring temperature, heavy castings	1900 — 2050°F

Uses

General utility bearing alloy
Bushings
Automobile fittings

HIGH-LEADED TIN BRONZE
A.S.T.M. B30-51 Alloy 3D
Nominal Composition: 78-7-15

*Chemical Analysis, per cent**

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P
Minimum	76.00[c]	6.50	14.00								
Nominal	78.00	7.00	15.00								
Maximum	79.00	7.50	16.00	0.75	0.75[c]	0.10	0.75	0.08	none[b]	0.003	0.03

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* For footnotes, see page 533.

HIGH-LEADED TIN BRONZE Nominal Composition: 78-7-15 (*Continued*)

Copper plus tin plus lead plus nickel must total a minimum of 98.50 per cent.

Physical Properties

Tensile strength, psi	25,000 — 33,000
Yield strength, psi	14,000 — 20,000
Elongation, per cent in 2 inches	10 — 18
Reduction of area, per cent	8 — 15
Modulus of elasticity, psi × 10^6	8.8 — 12.6
Brinell hardness (10-mm ball, 500-kg load)	50 — 60
Compression strength, psi:	
0.001 inch set	13,000 — 16,000
0.1 inch set	38,000 — 48,000
Impact strength (Izod), ft-lb	4 — 6
Specific gravity	9.10 — 9.40
Weight per cu inch, pounds	0.329 — 0.340
Patternmakers' shrinkage, inch per foot	3/16
Coefficient of thermal expansion (70—400°F)	0.0000103
Melting point	1700 — 1750°F
Pouring temperature, light castings	2000 — 2250°F
Pouring temperature, heavy castings	1900 — 2100°F

Uses

Locomotive engine castings and general service bearings for moderate pressure
Driving box, engine and trailer truck brasses, hub liners
General-purpose wearing metal for rod bushings, shoes, and wedges
Used in freight and street-car bearings
Backs for lined journal bearings for locomotive tenders, passenger cars, and freight equipment cars
A good bearing bronze, used largely where acid-resisting metal is required
Mine-water pump parts (corrosion-resisting)
Mining machinery
Bearings requiring lining metal for facing or lining
Rolling mill bearings
Brass and copper rolling mill neck bearings

HIGH-LEADED TIN BRONZE
A.S.T.M. B30-51 Alloy 3E
Nominal Composition: 70-5-25

Chemical Analysis, per cent[*]

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P
Minimum	69.00[c]	4.50	22.00								
Nominal	71.00	5.00	24.00								
Maximum	73.00	5.50	24.50	0.50	0.75[c]	0.10	0.75	0.08	none[b]	0.003	0.03

Copper plus tin plus lead plus nickel must total a minimum of 98.50 per cent.

Physical Properties

Tensile strength, psi	23,000 — 30,000
Yield strength, psi	11,000 — 15,000
Elongation, per cent in 2 inches	7 — 16
Reduction of area, per cent	5 — 12
Modulus of elasticity, psi × 10^6	9 — 12
Brinell hardness (10-mm ball, 500-kg load)	42 — 55

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[*] For footnotes, see page 533.

High-Leaded Tin Bronze Nominal Composition: 70-5-25 (*Continued*)

Compression strength, psi:	
0.001 inch set	12,000 — 14,000
0.1 inch set	22,000 — 25,000
Impact strength (Izod), ft-lb	4 — 6
Specific gravity	9.20 — 9.50
Weight per cu inch, pounds	0.332 — 0.343
Patternmakers' shrinkage, inch per foot	3/16
Melting point	1650 — 1700°F
Pouring temperature, light castings	2000 — 2200°F
Pouring temperature, heavy castings	1850 — 2000°F

Uses

Bearings operated at high speed and under light or medium pressure
Bronze for railroad bearings
Driving boxes
Special purpose where a soft metal is desired
Used extensively for railroad locomotive bearing parts

Leaded Red Brass

A.S.T.M. B30-51 Alloy 4A

Nominal Composition: 85-5-5-5

Chemical Analysis, per cent[*]

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P
Minimum	84.00[c]	4.25	4.50	4.50							
Nominal	85.00	5.00	5.00	5.00							
Maximum	85.50	5.25	5.50	5.75	0.75[c]	0.25	0.25	0.08	none[b]	0.003	0.03

Physical Properties

Tensile strength, psi	33,000 — 46,000
Yield strength, psi	17,000 — 24,000
Elongation, per cent in 2 inches	20 — 35
Reduction of area, per cent	17 — 32
Modulus of elasticity, psi $\times 10^6$	9.1 — 14.8
Brinell hardness (10-mm ball, 500-kg load)	55 — 65
Compression strength, psi:	
0.001 inch set	10,000 — 12,000
0.1 inch set	30,000 — 33,000
Impact strength (Izod), ft-lb	6 — 12
Specific gravity	8.7 — 8.88
Weight per cu inch, pounds	0.314 — 0.321
Patternmakers' shrinkage, inch per foot	3/16
Electrical conductivity, per cent I.A.C.S.	13 — 16.4
Thermal conductivity, per cent of Cu	16
Coefficient of thermal expansion (70—400°F)	0.0000109
Melting point	1810 — 1840°F
Solidification range	1830 — 1550°F
Pouring temperature, light castings	2100 — 2350°F
Pouring temperature, heavy castings	1950 — 2150°F

Uses

Known as "ounce metal," a high-grade red brass for general service
General castings requiring fair strength, soundness, and good machining qualities

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[*] For footnotes, see page 533.

LEADED RED BRASS Nominal Composition: 85-5-5-5 (*Continued*)

Castings used for hydrostatic pressures
Low-pressure valve bodies
Pipe fittings
Gasoline and oil-line fittings
Small pump castings
Water-pump impellers
Fire-equipment fittings
Plumbing goods
Trolley-line parts
Ornamental fixtures
Small gears

LEADED RED BRASS
A.S.T.M. B30-51 Alloy 4B
Nominal Composition: 83-4-6-7

*Chemical Analysis, per cent**

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P
Minimum	82.00[c]	3.50	5.75	6.00							
Nominal	83.00	4.00	6.00	7.00							
Maximum	83.50	4.25	6.75	7.50	0.75[c]	0.25	0.25	0.08	none[b]	0.003	0.01

Physical Properties

Tensile strength, psi	30,000 — 38,000
Yield strength, psi	12,000 — 17,000
Elongation, per cent in 2 inches	15 — 27
Reduction of area, per cent	12 — 25
Modulus of elasticity, psi × 10^6	12.5 — 15.5
Brinell hardness (10-mm ball, 500-kg load)	50 — 60
Compression strength, psi:	
0.001 inch set	11,000 — 12,000
0.1 inch set	28,000 — 30,000
Specific gravity	8.6 — 8.7
Weight per cu inch, pounds	0.311 — 0.314
Patternmakers' shrinkage, inch per foot	3/16
Melting point	1800°F
Pouring temperature, light castings	2100 — 2300°F
Pouring temperature, heavy castings	1950 — 2150°F

Uses

A general-purpose free-machining red brass alloy
Air, gas, and water fittings
Valves
Pipe fittings
Plumbers' supplies and specialties
Injectors
Common hydraulic pressure castings
Pumps and pump bodies
Hardware and fittings
Railroad catenary and overhead fittings
Carburetors

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* For footnotes, see page 533.

LEADED SEMI-RED BRASS
A.S.T.M. B30-51 Alloy 5A
Nominal Composition: 81-3-7-9

*Chemical Analysis, per cent**

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P
Minimum	79.50[c]	2.75	6.50	8.50							
Nominal	81.00	3.00	7.00	9.00							
Maximum	81.50	3.25	7.50	10.00	0.75[c]	0.35	0.20	0.08	none[b]	0.003	0.01

Physical Properties

Tensile strength, psi	29,000 — 39,000
Yield strength, psi	13,000 — 17,000
Elongation, per cent in 2 inches	18 — 30
Reduction of area, per cent	15 — 27
Modulus of elasticity, psi × 10^6	7.7 — 14.3
Brinell hardness (10-mm ball, 500-kg load)	50 — 60
Impact strength (Izod), ft-lb	6 — 10
Specific gravity	8.60 — 8.80
Weight per cu inch, pounds	0.311 — 0.318
Patternmakers' shrinkage, inch per foot	3/16
Electrical conductivity, per cent I.A.C.S.	18
Melting point	1750 — 1800° F
Pouring temperature, light castings	2100 — 2300° F
Pouring temperature, heavy castings	1950 — 2150° F

Uses

Sometimes referred to as "valve composition"
Low-pressure valves and fittings
General hardware fittings
Ornamental castings
Plumbing supplies and fixtures

LEADED SEMI-RED BRASS
A.S.T.M. B30-51 Alloy 5B
Nominal Composition: 76-3-6-15

*Chemical Analysis, per cent**

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P
Minimum	75.00[c]	2.75	5.50	14.00							
Nominal	76.00	3.00	6.00	15.00							
Maximum	76.75	3.25	6.50	16.00	0.50[c]	0.35	0.20	0.07	none[b]	0.005	0.01

Physical Properties

Tensile strength, psi	30,000 — 40,000
Yield strength, psi	12,000 — 16,000
Elongation, per cent in 2 inches	20 — 35
Reduction of area, per cent	15 — 30
Modulus of elasticity, psi × 10^6	10 — 14
Brinell hardness (10-mm ball, 500-kg load)	50 — 60
Compression strength, psi:	
0.001 inch set	8,000 — 10,000
0.1 inch set	29,000 — 32,000

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* For footnotes, see page 533.

Leaded Semi-Red Brass Nominal Composition: 76-3-6-15 (*Continued*)

Specific gravity	8.55 — 8.70
Weight per cu inch, pounds	0.309 — 0.314
Patternmakers' shrinkage, inch per foot	3/16
Melting point	1725 — 1775°F
Pouring temperature, light castings	2100 — 2300°F
Pouring temperature, heavy castings	1950 — 2150°F

Uses

Plumbing fixtures, cocks and faucets, stops and wastes
Air and gas fittings
General hardware fittings
Low-pressure valves and fittings

Leaded Yellow Brass
A.S.T.M. B30-51 Alloy 6A
Nominal Composition: 71-1-3-25

Chemical Analysis, per cent[*]

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P
Minimum	70.00	0.75	2.50	rem.							
Nominal	71.00	1.00	3.00	25.00							
Maximum	73.00	1.75	3.50	rem.	0.50	0.50	0.10	0.05	none[b]	0.05	0.01

Physical Properties

Tensile strength, psi	35,000 — 40,000
Yield strength, psi	12,000 — 14,000
Elongation, per cent in 2 inches	25 — 40
Reduction of area, per cent	20 — 40
Modulus of elasticity, psi × 10^6	11 — 14
Brinell hardness (10-mm ball, 500-kg load)	40 — 55
Compression strength, psi:	
0.001 inch set	8,000 — 10,000
0.1 inch set	28,000 — 32,000
Specific gravity	8.45 — 8.55
Weight per cu inch, pounds	0.305 — 0.309
Patternmakers' shrinkage, inch per foot	3/16 — 5/32
Electrical conductivity, per cent I.A.C.S.	15 — 22
Thermal conductivity, per cent of Cu	20 — 30
Coefficient of thermal expansion (70—200°F)	0.0000115
Melting point	1700 — 1750°F
Pouring temperature, light castings	2000 — 2100°F
Pouring temperature, heavy castings	1850 — 2000°F

Uses

Yellow brass alloy for general purposes
Yellow alloy for plumbers' fittings, fixtures, and trimming
Ferrules
Valves and fittings
Hardware
Ornamental work
Chandeliers
Andirons

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[*] For footnotes, see page 533.

LEADED YELLOW BRASS
A.S.T.M. B30-51 Alloy 6B
Nominal Composition: 67-1-3-29

Chemical Analysis, per cent[*]

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P
Minimum	66.00	0.75	2.75	rem.							
Nominal	67.00	1.00	3.00	29.00							
Maximum	69.00	1.25	3.50	rem.	0.50	0.50	0.10	0.05	none[b]	0.05	0.01

Physical Properties

Tensile strength, psi	30,000 — 38,000
Yield strength, psi	11,000 — 15,000
Elongation, per cent in 2 inches	20 — 35
Reduction of area, per cent	15 — 30
Modulus of elasticity, psi × 10^6	12 — 14
Brinell hardness (10-mm ball, 500-kg load)	40 — 60
Compression strength, psi:	
0.001 inch set	8,000 — 10,000
0.1 inch set	28,000 — 32,000
Specific gravity	8.40 — 8.50
Weight per cu inch, pounds	0.303 — 0.307
Patternmakers' shrinkage, inch per foot	3/16 — 7/32
Electrical conductivity, per cent I.A.C.S.	18 — 25
Coefficient of thermal expansion (70—200°F)	0.0000112
Melting point	1700 — 1725°F
Pouring temperature, light castings	1950 — 2100°F
Pouring temperature, heavy castings	1850 — 1950°F

Uses

General-purpose yellow casting alloy
Light castings not subject to high internal pressure
Furniture hardware
Ornamental castings
Hardware fittings
Radiator fittings
Ship trimmings
Gas cocks, coach trimmings, cast spray nozzles, light fixtures, battery clamps
Valves and fittings

LEADED YELLOW BRASS
A.S.T.M. B30-51 Alloy 6C
Nominal Composition: 60-1-1-38

Chemical Analysis, per cent

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P
Minimum	59.00	0.50	0.75	rem.					0.10		
Nominal	60.00	1.00	1.00	37.75					0.25		
Maximum	63.00	1.25	1.25	rem.	0.50	0.50	0.10	0.05	0.40	0.10	0.01

Physical Properties

Tensile strength, psi	40,000 — 45,000
Yield strength, psi	14,000 — 20,000

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[*] For footnotes, see page 533.

LEADED YELLOW BRASS Nominal Composition: 60-1-1-38 (*Continued*)

Elongation, per cent in 2 inches	15 — 25
Reduction of area, per cent	18 — 30
Modulus of elasticity, psi $\times 10^6$	13 — 15
Brinell hardness (10-mm ball, 500-kg load)	50 — 75
Specific gravity	8.30 — 8.47
Weight per cu inch, pounds	0.300 — 0.306
Patternmakers' shrinkage, inch per foot	1/4
Electrical conductivity, per cent I.A.C.S.	20 — 26
Coefficient of thermal expansion (70—500°F)	0.000012
Melting point	1675 — 1725°F
Pouring temperature, light castings	1950 — 2150°F
Pouring temperature, heavy castings	1800 — 2000°F

Uses

"Navy" yellow brass
Spring bushing alloy
Hardware
Fittings
Ornamental castings
Plumbers' flanges, scupper pipes, etc.
Ship trimmings

LEADED HIGH-STRENGTH YELLOW BRASS
A.S.T.M. B30-51 Alloy 7A
Tensile 60,000, Elongation 15 Per Cent

Chemical Analysis, per cent

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P
Minimum	56.00	0.50	0.50	rem.		0.75			0.25		
Maximum	62.00	1.00	1.00	rem.	0.50	1.50	0.05	0.05	1.00	0.10	0.005

Physical Properties

Tensile strength, psi	60,000 — 78,000
Yield strength, psi	25,000 — 40,000
Elongation, per cent in 2 inches	15 — 30
Reduction of area, per cent	15 — 30
Modulus of elasticity, psi $\times 10^6$	12 — 14
Brinell hardness (10-mm ball, 500-kg load)	80 — 95
Compression strength, psi:	
0.001 inch set	20,000 — 26,000
0.1 inch set	85,000 — 90,000
Impact strength (Izod), ft-lb	20 — 40
Specific gravity	8.0 — 8.4
Weight per cu inch, pounds	0.289 — 0.303
Patternmakers' shrinkage, inch per foot	7/32 — 1/4
Electrical conductivity, per cent I.A.C.S.	20 — 24
Coefficient of thermal expansion (70—400°F)	0.0000114
Melting point	1675 — 1725°F
Pouring temperature, light castings	1900 — 2050°F
Pouring temperature, heavy castings	1750 — 1900°F

Uses

Free-machining manganese bronze
Valve stems

LEADED HIGH-STRENGTH YELLOW BRASS Tensile 60,000, Elongation 15 Per Cent (*Cont.*)

Marine castings and fittings
Pump bodies
Gas-engine bases
Lever arms
Brackets
Gears

HIGH-STRENGTH YELLOW BRASS
(Manganese Bronze)
A.S.T.M. B30-51 Alloy 8A
Tensile 65,000, Elongation 20 Per Cent

Chemical Analysis, per cent

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P	Mn
Minimum	56.00			rem.		0.75			0.75			0.10
Maximum	59.00	1.00	0.30	rem.	0.50	2.00	0.01	0.05	1.50	0.03	0.005	1.00

Physical Properties

Tensile strength, psi	70,000 — 88,000
Yield strength, psi	28,000 — 40,000
Elongation, per cent in 2 inches	20 — 35
Reduction of area, per cent	20 — 40
Modulus of elasticity, psi × 10^6	13 — 15
Brinell hardness (10-mm ball):	
500-kg load	90 — 120
3,000-kg load	115 — 150
Compression strength, psi:	
0.001 inch set	22,000 — 26,000
0.1 inch set	85,000 — 90,000
Impact strength (Izod), ft-lb	20 — 40
Specific gravity	8 — 8.5
Weight per cu inch, pounds	0.289 — 0.307
Patternmakers' shrinkage, inch per foot	7/32 — 9/32
Electrical conductivity, per cent I.A.C.S.	16 — 20
Coefficient of thermal expansion (70—200°F)	0.000012
Melting point	1690°F
Solidification range	1660 — 1700°F
Pouring temperature, light castings	1900 — 2000°F
Pouring temperature, heavy castings	1750 — 1900°F

Uses

Substitute for steel and malleable iron castings
Propeller hubs and blades and other parts in contact with salt or fresh water
Valve stems, engine framing, complicated lever arms and parts of machinery requiring both strength and toughness
Gears
Liners

HIGH-STRENGTH YELLOW BRASS Tensile 65,000, Elongation 20 Per Cent (*Continued*)

- Hub caps
- Strength castings
- Bearings

HIGH-STRENGTH YELLOW BRASS
(Manganese Bronze)
A.S.T.M. B30-51 Alloy 8C
Tensile 110,000, Elongation 12 Per Cent

Chemical Analysis, per cent

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P	Mn
Minimum	60.00			rem.		2.00			4.00			3.00
Maximum	68.00	0.05	0.10	rem.	1.00	4.00	0.01	0.03	7.50	0.10	0.005	4.50

Physical Properties

Tensile strength, psi	110,000 — 120,000
Yield strength, psi	65,000 — 90,000
Elongation, per cent in 2 inches	12 — 18
Reduction of area, per cent	5 — 18
Modulus of elasticity, psi × 10^6	15 — 16.5
Brinell hardness (10-mm ball):	
500-kg load	170 — 225
3,000-kg load	190 — 235
Compression strength, psi:	
0.001 inch set	55,000 — 65,000
0.1 inch set	90,000 — 120,000
Impact strength (Izod), ft-lb	7 — 12
Specific gravity	7.7 — 8.0
Weight per cu inch, pounds	0.278 — 0.289
Patternmakers' shrinkage, inch per foot	5/16 — 1/4
Electrical conductivity, per cent I.A.C.S.	10 — 14
Thermal conductivity, per cent of Cu	12 — 14
Coefficient of thermal expansion (70—500°F)	0.000011
Melting point	1650 — 1700°F
Pouring temperature, light castings	1950 — 2150°F
Pouring temperature, heavy castings	1800 — 1950°F

Uses

- Extra heavy-duty high-strength alloy
- Spur gears
- Gibs
- Cams
- Bridge parts
- Large valve stems
- Gears
- Bearings (slow speed, heavy load)
- Screw-down nuts
- Hydraulic cylinder parts

ALUMINUM BRONZE
A.S.T.M. B30-51 Alloy 9A
Nominal Composition: 87½-3½-9

Chemical Analysis, per cent

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P	Mn
Minimum	86.00					3.00			8.50			
Nominal	87.50					3.50			9.00			
Maximum	88.00	0.10	0.05	0.10	0.25	4.00	0.01	0.05	9.50	0.15	0.005	0.25

Copper, iron, aluminum, nickel, and manganese must total 99.5 per cent.

Physical Properties

Tensile strength, psi	70,000 — 87,000
Yield strength, psi	25,000 — 30,000
Elongation, per cent in 2 inches	22 — 38
Reduction of area, per cent	20 — 36
Modulus of elasticity, psi × 10^6	16 — 18
Brinell hardness (10-mm ball):	
500-kg load	90 — 125
3,000-kg load	110 — 140
Compression strength, psi:	
0.001 inch set	27,000 — 31,000
0.1 inch set	65,000 — 70,000
Impact strength (Izod), ft-lb	35 — 50
Specific gravity	7.3 — 7.50
Weight per cu inch, pounds	0.264 — 0.271
Patternmakers' shrinkage, inch per foot	5/16 — 11/32
Electrical conductivity, per cent I.A.C.S.	12 — 14
Thermal conductivity, per cent of Cu	12 — 14
Coefficient of thermal expansion (70—250°F)	0.0000095
Pouring temperature, light castings	2050 — 2200°F
Pouring temperature, heavy castings	2000 — 2100°F

Uses

General utility aluminum bronze maintaining strength at elevated temperatures
Resistant to mild but not to strong alkalies
Acid-resisting pump parts
Pickling tank castings and baskets
Valve seats, valve guides, valve stems
Marine equipment, propellers
Worm wheels
Welding jaws
Bearings and bushings
This alloy has high corrosion resistance to many chemicals. For specific application, contact supplier.

ALUMINUM BRONZE
A.S.T.M. B30-51 Alloy 9B
Nominal Composition: 89-1-10

Chemical Analysis, per cent

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P	Mn
Minimum	86.00					0.75			9.00			
Nominal	89.00					1.00			10.00			
Maximum	90.00	0.10	0.05	0.10	0.25	1.50	0.01	0.05	11.00	0.15	0.005	0.25

Copper, iron, aluminum, nickel, and manganese must total 99.5 per cent.

Aluminum Bronze Nominal Composition: 89-1-10 (*Continued*)

Physical Properties

	As Cast	As Heat Treated
Tensile strength, psi	70,000 — 85,000	80,000 — 95,000
Yield strength, psi	30,000 — 35,000	40,000 — 55,000
Elongation, per cent in 2 inches	20 — 35	12 — 16
Reduction of area, per cent	15 — 30	12 — 16
Modulus of elasticity, psi × 10^6	14 — 16	15 — 18.5
Brinell hardness (10-mm ball):		
500-kg load	100 — 140	
3,000-kg load	110 — 160	160 — 225
Compression strength, psi:		
0.001 inch set	16,000 — 20,000	35,000 — 45,000
0.1 inch set	75,000 — 83,000	
Impact strength (Izod), ft-lb	30 — 36	22 — 27
Specific gravity	7.3 — 7.65	
Weight per cu inch, pounds	0.264 — 0.276	
Patternmakers' shrinkage, inch per foot	5/16 — 7/32	
Electrical conductivity, per cent I.A.C.S.	12 — 15	13.8
Thermal conductivity, per cent of Cu	14 — 15	
Coefficient of thermal expansion (70—500°F)	0.0000091—98	0.0000097
Pouring temperature, light castings	2050 — 2200°F	
Pouring temperature, heavy castings	1950 — 2100°F	

Uses

General-purpose aluminum bronze subject to heat treatment, maintaining strength at elevated temperatures
Resistant to mild but not to strong alkalies
Pickling baskets
Steel-mill stripper nuts, slippers and heavy-duty feed nuts
Spur helical, bevel, internal gears
Valve seats
Bushings and bearings
Marine equipment
Welding jaws
This alloy has high corrosion resistance to many chemicals. For specific application, contact supplier

Aluminum Bronze
A.S.T.M. B30-51 Alloy 9C
Nominal Composition: 85-4-11

Chemical Analysis, per cent

	Cu	Fe	Al	Ni	Mn	Others
Minimum	83.00	3.00	10.00			
Maximum		5.00	11.50	2.50	0.50	0.50

Copper, iron, aluminum, nickel, and manganese must equal 99.50 per cent.

Physical Properties

	As Cast	As Heat Treated
Tensile strength, psi	75,000 — 95,000	90,000 — 110,000
Yield strength, psi	30,000 — 41,000	45,000 — 52,000
Elongation, per cent in 2 inches	12 — 20	6 — 15
Reduction of area, per cent	12 — 20	7 — 18
Modulus of elasticity, psi × 10^6	16 — 20	15 — 19.5
Brinell hardness (10-mm ball, 3000-kg load)	150 — 185	190 — 235
Impact strength (Izod), ft-lb	7 — 22	

ALUMINUM BRONZE Nominal Composition: 85-4-11 *(Continued)*

Specific gravity	7.52
Weight per cu inch, pounds	0.272
Patternmakers' shrinkage, inch per foot	5/16 — 7/32
Electrical conductivity, per cent I.A.C.S.	12
Thermal conductivity, per cent of Cu	18
Coefficient of thermal expansion (70—500°F)	0.00009
Melting point	1880 — 1900°F
Solidification range	1850 — 1910°F
Pouring temperature, light castings	2300°F
Pouring temperature, heavy castings	2150°F

Uses

Gears
Worm wheels
Bushings
Pump parts
Propeller blade bushings
Valve seats
Landing-gear parts

LEADED NICKEL BRASS (NICKEL SILVER)
A.S.T.M. B30-51 Alloy 10A
Nominal Composition: 57-2-9-20-12

*Chemical Analysis, per cent**

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P	Mn
Minimum	55.00	1.50	8.00	rem.	11.00							
Nominal	57.00	2.00	9.00	20.00	12.00							
Maximum	58.00	2.50	10.00	rem.	13.00	1.00	0.25	0.05	none[b]	0.01	0.05	0.50

Physical Properties

Tensile strength, psi	30,000 — 40,000
Yield strength, psi	15,000 — 20,000
Elongation, per cent in 2 inches	10 — 25
Reduction of area, per cent	7 — 20
Modulus of elasticity, psi × 10^6	15 — 16.5
Brinell hardness (10-mm ball, 500-kg load)	50 — 60
Specific gravity	8.80 — 8.90
Weight per cu inch, pounds	0.318 — 0.322
Patternmakers' shrinkage, inch per foot	1/8 — 3/16
Electrical conductivity, per cent I.A.C.S.	5 — 7
Thermal conductivity, per cent of Cu	7.3
Pouring temperature, light castings	2200 — 2400°F
Pouring temperature, heavy castings	2000 — 2200°F

Uses

A free-machining leaded nickel brass
Hardware fittings
Valves
Valve trimmings
Plumbing fixtures
Statuary
Ornamental castings

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* For footnotes, see page 533.

Leaded Nickel Brass (Nickel Silver)
A.S.T.M. B30-51 Alloy 10B
Nominal Composition: 60-3-5-16-16

*Chemical Analysis, per cent**

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P	Mn
Minimum	58.00	2.50	4.50	rem.	15.50							
Nominal	60.00	3.00	5.00	16.00	16.00							
Maximum	61.00	3.50	5.50	rem.	17.00	1.00	0.25	0.05	none[b]	0.03	0.05	0.50

Physical Properties

Tensile strength, psi	35,000 — 45,000
Yield strength, psi	17,000 — 24,000
Elongation, per cent in 2 inches	15 — 30
Reduction of area, per cent	15 — 30
Modulus of elasticity, psi × 10^6	....
Brinell hardness (10-mm ball, 500-kg load)	65 — 80
Specific gravity	8.80 — 8.90
Weight per cu inch, pounds	0.318 — 0.322
Patternmaker's shrinkage, inch per foot	3/16
Electrical conductivity, per cent I.A.C.S.	5 — 6
Thermal conductivity, per cent of Cu	7.0
Pouring temperature, light castings	2250 — 2450°F
Pouring temperature, heavy castings	2050 — 2250°F

Uses

A free-machining leaded nickel brass
Valves
Valve fittings and trimmings
Pipe fittings
Plumbers' fittings and fixtures
Hardware
Boat and railroad car fittings
Ornamental castings
Statuary

Leaded Nickel Bronze (Nickel Silver)
A.S.T.M. B30-51 Alloy 11A
Nominal Composition: 64-4-4-8-20

*Chemical Analysis, per cent**

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P	Mn
Minimum	63.00	3.50	3.50	rem.	19.50							
Nominal	64.00	4.00	4.00	8.00	20.00							
Maximum	65.00	4.50	5.00	rem.	21.00	1.00	0.25	0.05	none[b]	0.05	0.05	1.00

Copper, tin, lead, zinc, nickel, and manganese must total 99 per cent

Physical Properties

Tensile strength, psi	40,000 — 60,000
Yield strength, psi	17,000 — 30,000
Elongation, per cent in 2 inches	15 — 25
Reduction of area, per cent	11 — 22
Modulus of elasticity, psi × 10^6	17 — 18

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* For footnotes, see page 533.

Leaded Nickel Bronze (Nickel Silver) Nominal Composition: 64-4-4-8-20 (*Cont.*)

Brinell hardness (10-mm ball, 500-kg load)	76 — 120
Impact strength (Izod), ft-lb	....
Specific gravity	8.80 — 8.90
Weight per cu inch, pounds	0.318 — 0.322
Patternmakers' shrinkage, inch per foot	3/16
Electrical conductivity, per cent I.A.C.S.	4.5 — 5.5
Thermal conductivity, per cent of Cu	6.0
Pouring temperature, light castings	2300 — 2600°F
Pouring temperature, heavy castings	2250 — 2400°F

Uses

Free-machining leaded nickel bronze
Valves
Marine castings
Fittings
Ship trimmings
Furniture trim
Hardware
Building trim
Ornamental castings

Leaded Nickel Bronze (Nickel Silver)
A.S.T.M. B30-51 Alloy 11B
Nominal Composititon: 66-5-1½-2-25

*Chemical Analysis, per cent**

	Cu	Sn	Pb	Zn	Ni	Fe	Sb	S	Al	Si	P	Mn
Minimum	64.00	4.00	1.00	rem.	24.00							
Nominal	66.50	5.00	1.50	2.00	25.00							
Maximum	67.00	5.50	2.00	rem.	26.00	1.00	0.25	0.05	none[b]	0.10	0.05	1.00

Physical Properties

Tensile strength, psi	50,000 — 65,000
Yield strength, psi	26,000 — 40,000
Elongation, per cent in 2 inches	15 — 25
Reduction of area, per cent	15 — 30
Modulus of elasticity, psi × 10^6	19 — 22
Brinell hardness, (10-mm ball, 500-kg load)	120 — 150
Impact strength (Izod), ft-lb	....
Specific gravity	8.80 — 8.90
Weight per cu inch, pounds	0.318 — 0.322
Patternmakers' shrinkage, inch per foot	3/16
Electrical conductivity, per cent I.A.C.S.	4 — 5
Thermal conductivity, per cent of Cu	6.5
Pouring temperature, light castings	2400 — 2600°F
Pouring temperature, heavy castings	2300 — 2400°F

Uses

Corrosion-resistant alloy for some organic liquids
Dairy and soda-fountain parts
Valves and valve seats for elevated temperatures
Ornamental castings
Hardware
Musical instrument keys
A permanently white nickel bronze

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* For footnotes, see page 533.

Footnotes to chemical analysis tabulations:

(*a*) By agreement between the manufacturer and the purchaser, a definite nickel content up to 0.80 per cent may be specified. In such case the nickel shall be within plus or minus 0.20 per cent of the desired content, and an analysis shall be made for it.

(*b*) The term "none" as applied to aluminum allowance is defined as 0.005 per cent, determined on a 10-gram sample.

(*c*) In determining copper, minimum copper may be computed as copper plus nickel.

CONFORMING SPECIFICATIONS FOR COPPER ALLOY CASTINGS

Specifications covering castings of copper-base alloys are given in the Manual of the Brass and Bronze Ingot Institute. Similar specifications, varying only in minor details, are issued by the American Society for Testing Materials. The latter are published in the "Nonferrous Metals" volume of that Society as issued triennially, with yearly supplements. All specifications for brass and bronze castings and ingots are also published in a separate yearly volume, "ASTM Standards on Copper and Copper Alloys." Each of the individual specifications may also be obtained as an individual leaflet.

Army, Navy, Military, and Federal Specifications

All new and revised Army-Navy specifications are now being issued as Military (MIL). Army, Army Air Forces, Navy Bureau of Aeronautics, some Navy bureaus, and other Government departments except the Navy generally, use Federal specifications for procurement. The Bureau of Ships, however, uses the Navy Department specifications. An index to these specifications is also published quarterly by the Government Printing Office, and this index includes the "MIL" specifications.

The Society of Automotive Engineers issues their specifications as a year book. The nonferrous section of this book is published as a separate leaflet. The Aeronautical Material Specifications (A.M.S. Series) are also published by the S.A.E. and an index of them or a copy of any individual specification can be purchased from the Society.

Addresses from which the above specifications may be obtained are as follows:

A.S.T.M.: American Society for Testing Materials, 1916 Race Street, Philadelphia 3, Pa.
B.B.I.I.: Brass and Bronze Ingot Institute, 308 W. Washington Street, Chicago, Ill.
Federal-Military: Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C.
Navy: Bureau of Supplies and Accounts, Navy Dept., Washington 25, D. C.
S.A.E.: Society of Automotive Engineers, Inc., 29 W. 39th Street, New York 18, N. Y.

A.M.S.: Aeronautical Materials Specifications of the S.A.E., 29 W. 39th St., New York 18, N. Y.

References

1. "Ingot Brass and Bronze Manual," Brass and Bronze Ingot Institute, Chicago, 1951. Most of the information in this chapter was taken from this source.
2. Wolf, F. L., "Ingot Metal versus Virgin Metal," *Trans. Am. Foundrymen's Soc.*, 56 (1948); *Am. Foundryman*, 13, 94-6 (May, 1948).

Chapter 25

Wrought Copper Alloys

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The wide variety of wrought alloys made possible by the many elements that can be alloyed with copper confronts the writer with a myriad of problems in selection. The wrought alloys given attention in these pages comprise most of those in regular quantity production in the brass mills—the principal source of copper alloys in wrought form—and the selection of properties includes those found to be of most interest to both producers and consumers.

In presenting the subject matter of this chapter, the principal aim has been the tabulation of individual alloys, compositions, and properties in an arrangement and grouping thought to be of most value. For further detail, reference to "The Metals Handbook[1]" is suggested. One of the best sources for quickly identifying the great number of trade names in use throughout the metal industry is the volume compiled by Woldman and Metzler[2]. For authoritative and up-to-date information on standardization in the production of mill products and on their properties, publications issued by the Copper and Brass Research Association and the various manufacturers should be consulted. Wilkins and Bunn[3] have compiled extensive data, given primarily in curve-chart form, on the effect of heating and working on physical properties.

General

The wrought alloys of copper are regarded as only those made by alloying the various components and casting into slabs, cakes, or billets for rolling, drawing, extrusion, or forging. Certain types of copper made at the copper refineries could, in the strict sense, be called alloys; these have been described in the chapters devoted to copper. Unless the amount of alloying element modifies the properties substantially, the material is not ordinarily classed as an alloy. The dividing line between commercially pure copper and its alloys is not sharp, either by definition or by usage.

The range of chemical compositions for the wrought alloys of copper is narrower than for the casting alloys. Many compositions that can be poured successfully into either sand or permanent molds are entirely unfit for working operations. In rolling, drawing, forging, extrusion, or tube-billet piercing a high degree of ductility or malleability, either hot or cold, is a prime requisite. Nevertheless, the many elements that can be allowed with copper, singly or in combination, through wide ranges in percentage, have resulted in the commercial production of a great number of individual compositions. Depending on the alloy, the products of the brass mills comprise such diverse shapes as plate, sheet, strip, bar, rod, wire, and seamless tube.

The chief elements alloyed with copper are zinc, tin, lead, nickel, silicon, and aluminum, and to a lesser extent manganese, cadmium, iron, phosphorus, arsenic, chromium, beryllium, selenium, and tellurium.

Compositions

Although there are several hundred wrought copper alloys available commercially, and although advances in metallurgy have brought about the constant development of new alloys and groups of alloys, the total number of individual compositions in production now is probably less than twenty-five years ago. Industry has found in many cases that minor variations in chemical composition could be combined into one alloy having adequate properties for certain applications or fields of use.

In the brass-mill industry, the wrought alloys of copper are, in general, designated by names established through long usage; in other words, the industry uses what might be called essentially a word-nomenclature system. Because the more important alloying elements can be used effectively in various proportions, the alloys are readily classified into a number of well-recognized groups as indicated by the chemical compositions listed in Table 25-1. During the past twenty years it has increasingly become the practice for manufacturers to publish the nominal or intended chemical compositions of their alloys. The permissible composition ranges or tolerances from the nominal, and the tolerances for various impurities, are made a part of the requirements in standard specifications for brass-mill products.

There is good reason for disclosing full information on chemical composition in conjunction with the alloy name. For although many of the names have had long usage, in some instances the chemical compositions have been modified or adjusted from time to time to fit changes in mill practice or in the needs of consumers. Producers often designate their

TABLE 25-1. COMPOSITION AND FORMS

Name	Nominal Composition, Per Cent					Typical Forms*
	Copper	Zinc	Lead	Tin	Others	
Brasses—Nonleaded						
Gilding, 95%	95.00	5.00				S, W
Commercial bronze, 90%	90.00	10.00				S, R, W, T
Red brass, 85%	85.00	15.00				S, R, W, T
Low brass, 80%	80.00	20.00				S, R, W
Cartridge brass, 70%	70.00	30.00				S, R, W, T
Yellow brass, 66%	66.00	34.00				S, W
Yellow brass, 63%	63.00	37.00				R, W
Muntz metal	60.00	40.00				S, T
Leaded Brasses						
Leaded commercial bronze	89.00	9.25	1.75			R
Leaded tube brass	66.50	33.00	0.50			T
High-leaded tube brass	66.50	31.90	1.00			T
Low-leaded brass	64.50	35.00	0.50			S
Medium-leaded brass	64.50	34.50	1.00			S, R, W
High-leaded brass	64.00	34.00	2.00			S, R
Free-cutting brass	61.50	35.25	3.25			R
Leaded Muntz metal	60.00	39.40	0.60			P
Free-cutting Muntz metal	60.00	39.00	1.00			T
Forging brass	60.00	38.00	2.00			R, F
Architectural bronze	56.00	41.50	2.50			ES
Tin and Aluminum Brasses						
Inhibited admiralty**	71.00	28.00		1.00		P, T
Naval brass	60.00	39.25		0.75		P, S, R, W, T, F
Leaded naval brass	60.00	37.50	1.75	0.75		R, F
Manganese bronze, (A)	58.50	39.20		1.00	Mn 0.30 Fe 1.00	P, R, F
Aluminum brass**	77.00	21.00			Al 2.00	T
** Arsenic, antimony, or phosphorus 0.02 to 0.10.						
Phosphor Bronzes						
Phosphor bronze, 5% (A)	94.75			5.00	P 0.25	S, R, W, T
Phosphor bronze, 8% (C)	91.75			8.00	P 0.25	S, R, W
Phosphor bronze, 10% (D)	89.75			10.00	P 0.25	S, R, W
Phosphor bronze, 1.25% (E)	98.70			1.25	P 0.05	S
Leaded phosphor bronze	93.90		1.00	5.00	P 0.10	S, R
Free-cutting phosphor bronze	87.90	4.00	4.00	4.00	P 0.10	R
Cupronickels						
Cupronickel, 10%	88.35		10.00	1.25	Mn 0.40	P, T
Cupronickel, 30%	68.00		30.00	0.50	Mn 0.60	P, R, T
Nickel Silvers						
Nickel silver, 65-18	65.00	17.00	18.00			S, R, W
Nickel silver, 55-18	55.00	27.00	18.00			S, R, W
Nickel silver, 65-12	65.00	23.00	12.00			S, W
Nickel silver, 65-10	65.00	25.00	10.00			S, W
Silicon Bronzes (Copper-Silicon Alloys)						
High-silicon bronze (A)	95.80				Si 3.10 Mn 1.10***	S, R, W, T, F
Low-silicon bronze (B)	98.25				Si 1.50 Mn 0.25***	S, R, W, T
*** In place of manganese, iron or zinc are also used in comparable amounts.						
Aluminum Bronzes						
Aluminum bronze, 5%	95.00				Al 5.00	S, R, T
Aluminum bronze, 8%	92.00				Al 8.00	S, R
Aluminum bronze, (D)	90.25			2.75	Al 7.00	P, S
Aluminum bronze, (E)	82.00		5.00	2.50	Al 9.50 Mn 1.00	P, R
Aluminum-silicon bronze	90.75				Al 7.25 Si 2.00	R, F
Other Copper Alloys						
Cadmium bronze	99.00				Cd 1.00	W
Chromium copper	99.05				Cr 0.85 Si 0.10	R
Beryllium copper	97.70 (Ni + Co + Fe 0.40)				Be 1.90	S, R, W
Leaded copper	99.00				Pb 1.00	R
Selenium copper	99.40				Se 0.60	R

*S = sheet and strip R = rod W = wire T = tube P = plate
F = forgings ES = extruded shapes

alloys by a system of manufacturers' alloy numbers; this serves the double purpose of identifying metal going through the mill and of having a distinguishing designation for the customer's use in identifying the material as the product of that particular producer. Since these systems vary with each manufacturer and because some of the names do not have universal acceptance, the chemical composition is the one positive common denominator.

In this chapter, the alloy groups are designated brasses (nonleaded), leaded brasses, tin and aluminum brasses, phosphor bronzes, cupronickels, nickel silvers, silicon bronzes (copper-silicon alloys), aluminum bronzes, and other alloys.

Observations on the Effects of Alloying Elements

A discussion of the effects of the various alloying elements on the properties of the alloys becomes essentially an enumeration of some of the general characteristics of each of the alloy groups.

Zinc is by far the most important alloying element in copper alloys. It is used in substantial proportions in the three groups of brasses which account for half of the alloys listed in Table 25-1, and also in the nickel silvers. As might be expected, the brass alloys account for a major portion of the total brass-mill production. Most of the brasses are within the alpha field of the phase diagrams, thus maintaining good cold-working properties. With a higher zinc content of about 40 per cent, the beta phase facilitates hot working. The addition of zinc decreases the melting point, the density, the electrical and thermal conductivities, and the modulus of elasticity; it increases the coefficient of expansion, the strength, and hardness. Work hardening increases with zinc content, but binary 70-30 brass has the best combination of strength and ductility. In those alloys where it is not added as an alloying element, zinc is an impurity that is held to a controlled maximum.

Lead is added to about a third of the copper alloys in amounts ranging up to 4 per cent, the limit for good working qualities. In the solid state, it does not dissolve appreciably in the copper alloys but remains distributed as particles of free lead. Its principal function is to make the alloys free-cutting in machining operations; it has a somewhat similar effect in improving the blanking qualities of strip. Lead increases the density and decreases conductivity in direct proportion to the amount present. In nonleaded alloys, it is an unwanted impurity, held to a few hundredths of a per cent because of its pronounced harmful effect on the ductility needed for severe working operations. In cartridge brass to be hot rolled, the lead content must be not more than 0.01 per cent. In certain alloys, particularly nickel silver, lead must not be more than 0.02 per cent for best working qualities.

Tin is the essential alloying element in the phosphor bronze group of alloys. The maximum limit for tin is about 10 per cent in alloys that are to be cold worked, and up to this amount the copper-tin alloys are of alpha grain structure. The addition of tin to copper increases the strength and hardness at a rapid rate, and reduces the melting point, density, and electrical and thermal conductivities. Tin is added to some of the brasses in amounts of about 1 per cent for improving resistance to corrosion by dezincification in sea water, as in admiralty, naval brass, and manganese bronze. Tin is particularly beneficial in providing the high elastic limit, resilience, and endurance strength characteristic of springs made from phosphor bronze. Small additions of tin to some of the brasses high in copper content have a similar, although lesser, effect.

Nickel is the significant alloying element in the cupronickels. One of its most pronounced and most evident effects is the change in color of the alloy as the nickel content increases. The color of cupronickel is almost nickel-white. The addition of nickel to copper increases the strength and hardness, but the work-hardening qualities imparted by this element are less than for the other common alloying elements in copper. Nickel has a very pronounced effect in decreasing the electrical and thermal conductivities, and also slightly lowers the coefficient of thermal expansion. It increases the modulus of elasticity substantially. Being of about the same density as copper, it has practically no effect on this property. Although nickel and copper are mutually soluble in all proportions in the solid state, 30 per cent is the maximum nickel content for alloys that can be manufactured with brass-mill equipment. Beyond 30 per cent nickel the melting points and annealing temperatures reach values that are too high for the furnaces, and the resistance to cold work becomes too great for customary brass-mill reduction schedules. Cupronickels are particularly suitable for service at elevated temperatures. In the nickel silvers, the various combinations of nickel and zinc provide a wide assortment of alloys in various silvery-white color shades having working properties that approach the readily fabricated brasses.

Silicon can be present in wrought copper alloys in amounts up to 3 per cent, the limit for obtaining alpha-phase alloys of good working qualities. The addition of silicon increases the rate of work hardening very rapidly, although in soft temper ductility is outstandingly high, as indicated by elongation in the tension test. Silicon decreases the melting point, the density, and the electrical and thermal conductivities. The excellent welding qualities of the copper-silicon alloys, or silicon bronzes, have had a large part in establishing this relatively new group of alloys in commercial applications.

Aluminum serves as the essential alloying element in the group of aluminum bronzes. In wrought form, the alloys are limited to about 10 per cent aluminum content, with cold-working alloys held to 8 per cent or less for ductile alpha structure. All of the aluminum bronzes can be hot worked, and in the range from 8 to 10 per cent aluminum the beta phase facilitates hot rolling, forging, and extrusion. Aluminum decreases the melting point, electrical conductivity, and thermal conductivity; it has a pronounced effect in decreasing the density to values that are substantially below those for other copper alloys.

Manganese is used in some of the wrought copper alloys principally as a subordinate or secondary alloying element. In manganese bronze, and also in the aluminum bronzes, it improves the grain structure. It is added to the cupronickels and nickel silvers in small amounts to improve the metal quality in mill shapes for working operations, and its presence is permitted but not required in the finished product. In the copper-silicon alloys, manganese improves the grain structure and welding qualities. This element reduces the electrical conductivity drastically, making it useful in a few copper-manganese alloys of very high electrical resistivity and low temperature coefficient of resistivity.

The use of phosphorus in copper alloys is confined almost entirely to the phosphor bronzes, where it is present in amounts up to 0.50 per cent. It serves as a deoxidizer in making these copper-tin alloys, and the residual phosphorus content increases the mechanical properties. In admiralty and aluminum brass, phosphorus is used as one of the inhibitors of dezincification. Phosphorus is extremely potent in reducing electrical conductivity; however, when used in combination with small amounts of nickel to form nickel phosphide, the phosphide can be precipitated by heat treatment to improve the strength substantially, and because it is not in solid solution the phosphorus ceases to affect conductivity appreciably. Phosphorus is also used in some of the high-copper alloys of copper-zinc-tin for the same reasons as in phosphor bronze. If present as an impurity in brass, this element markedly affects grain growth and thereby disrupts annealing schedules.

Iron is used only as a minor alloying element in amounts up to 2.5 per cent, and in but a few of the copper alloys. In manganese bronze, and whenever it is present in the aluminum bronzes and silicon bronzes, it makes a finer-grained alloy and adds strength. In small amounts it is added to the cupronickels for improved resistance to corrosion by sea water. Iron is present as an impurity in all copper alloys and when the contamination of the alpha brasses becomes excessive, to a point beyond the usual 0.05 per cent limit, the resulting effect on grain growth may disturb annealing schedules. Although copper alloys are considered nominally nonmagnetic, the amount of iron present as impurity or added element does affect the magnetic susceptibility to an extent that must be taken into account if the alloys are to be used for magnetic-instrument construction. Butts and Reiber[4] conducted an extensive laboratory investigation in this field to determine the effect of iron content and heat treatment on magnetism (see Chapter 23).

The use of arsenic in wrought copper alloys is confined almost entirely to its function as an inhibitor of dezincification corrosion in admiralty and aluminum brass, where it is present to the extent of a few hundredths of a per cent.

Cadmium can be added to copper in amounts up to 1 per cent and still obtain a composition that is sufficiently ductile and malleable for mill working operations. Its value as an alloying element is due to its ability to increase the strength and wearing qualities of copper moderately with less sacrifice of electrical conductivity than when other alloying elements are used to obtain the same strength. This combination of properties makes the copper-cadmium alloys especially suitable for trolley wire, long-span power lines, and similar applications. The same advantages make these alloys adaptable to various types of welding electrodes used for electrical resistance welding.

The addition of 0.8 per cent chromium and a small amount of silicon to copper provides an alloy that can be softened for working operations by a high-temperature anneal and quench, and then substantially increased in strength, hardness, and electrical conductivity by a relatively low-temperature precipitation heat treatment.

Beryllium is added to copper in amounts up to about 2 per cent to obtain precipitation-hardening alloys of strength and hardness far beyond any of the other copper alloys. Softening for cold working is accomplished by annealing and quenching from a high temperature. The age-hardening or precipitation-hardening heat treatment at relatively low temperatures is applied subsequent to working operations. Cobalt is sometimes employed in combination with beryllium in such alloys.

Either selenium or tellurium can be added to copper in small amounts to obtain a type of slightly alloyed copper that is free-machining and hot-workable, at the same time retaining the essential strength and conductivity of copper.

Physical Properties

For the wrought alloys of copper, some of the physical properties of most general interest are listed in Table 25-2, which tabulates melting

TABLE 25-2. PHYSICAL PROPERTIES

Name	Melting Point, °C Liquidus	Melting Point, °C Solidus	Density, lb per cu in.	Specific Gravity	Coefficient of Thermal Expansion per °F (from 77 to 572°F)	Electrical Resistivity, ohms (mil, ft) at 68°F (Annealed)	Electrical Conductivity, per cent IACS at 68°F (Annealed)	Thermal Conductivity, Btu/sq ft/ft/hr/°F at 68°F
Brasses—Nonleaded								
Gilding, 95%	1065	1050	0.320	8.86	0.0000100	18.5	56	135
Commercial bronze, 90%	1045	1020	0.318	8.80	0.0000102	23.5	44	109
Red brass, 85%	1025	990	0.316	8.75	0.0000104	28	37	92
Low brass, 80%	1000	965	0.313	8.67	0.0000106	32	32	81
Cartridge brass, 70%	955	915	0.308	8.53	0.0000111	37	28	70
Yellow brass, 66%	930	905	0.306	8.47	0.0000113	38	27	67
Yellow brass, 63%	920	920	0.305	8.44	0.0000114	40	26	69
Muntz metal	905	900	0.303	8.39	0.0000116	37	28	71
Leaded Brasses								
Leaded commercial bronze	1040	1010	0.319	8.83	0.0000102	25	42	104
Leaded tube brass	940	905	0.307	8.50	0.0000112	40	26	67
High-leaded tube brass	930	900	0.308	8.53	0.0000113	40	26	67
Low-leaded brass	925	900	0.306	8.47	0.0000113	40	26	67
Medium-leaded brass	925	885	0.306	8.47	0.0000113	40	26	67
High-leaded brass	910	885	0.306	8.47	0.0000113	40	26	67
Free-cutting brass	900	885	0.307	8.50	0.0000114	40	26	67
Leaded Muntz metal	900	885	0.304	8.41	0.0000116	38	28	71
Free-cutting Muntz metal	900	885	0.304	8.41	0.0000116	38	27	69
Forging brass	895	880	0.305	8.44	0.0000115	38	27	69
Architectural bronze	890	875	0.306	8.47	0.0000116	37	28	71
Tin and Aluminum Brasses								
Inhibited admiralty	935	900	0.308	8.53	0.0000112	42	25	64
Naval brass	900	885	0.304	8.40	0.0000118	40	26	67
Leaded naval brass	900	885	0.305	8.44	0.0000118	40	26	67
Manganese bronze, (A)	890	865	0.302	8.36	0.0000118	43	24	61
Aluminum brass	970	935	0.301	8.33	0.0000103	45	23	58

Phosphor Bronzes								
Phosphor bronze, 5% (A)	1050	950	0.320	8.86	0.0000099	58	18	47
Phosphor bronze, 8% (C)	1020	880	0.318	8.80	0.0000101	80	13	36
Phosphor bronze, 10% (D)	1000	845	0.317	8.78	0.0000102	94	11	29
Phosphor bronze, 1.25% (E)	1075	1035	0.321	8.89	0.0000099	22	48	120
Leaded phosphor bronze	1050	920	0.322	8.91	0.0000099	58	18	48
Free-cutting phosphor bronze	1000	930	0.320	8.86	0.0000096	55	19	50
Cupronickels								
Cupronickel, 10%	1145	1105	0.323	8.94	0.0000093	113	9.2	26
Cupronickel, 30%	1240	1170	0.323	8.94	0.0000090	225	4.6	17
Nickel Silvers								
Nickel silver, 65-18	1110	1070	0.316	8.75	0.0000090	170	6	19
Nickel silver, 55-18	1055	1000	0.314	8.70	0.0000093	190	5.5	17
Nickel silver, 65-12	1040	1000	0.314	8.70	0.0000090	130	8	23
Nickel silver, 65-10	1020	985	0.313	8.67	0.0000091	115	9	26
Silicon Bronzes (Copper-Silicon Alloys)								
High-silicon bronze, (A)	1025	970	0.308	8.53	0.0000100	160	6.5	19
Low-silicon bronze, (B)	1060	1030	0.316	8.75	0.0000099	94	11	31
Aluminum Bronzes								
Aluminum bronze, 5%	1072	1062	0.295	8.17	0.0000099	61	17	46
Aluminum bronze, 8%	1045	1037	0.281	7.78	0.0000099	70	14.8	41
Aluminum bronze, (D)	—	—	0.285	7.89	0.000009	81	12.8	36
Aluminum bronze, (E)	1055	—	0.274	7.58	0.000009	138	7.5	22
Aluminum-silicon bronze	1005	985	0.278	7.69	0.000010	113	9.2	26
Other Copper Alloys								
Cadmium bronze	1075	1025	0.321	8.89	0.0000098	11.9	87	199
Chromium copper	1075	—	0.321	8.89	0.0000098	26*, 13	40*, 80	99*, 187
Beryllium copper	955	864	0.297	8.22	0.0000093**	60*, 35	17*, 30	46*, 60
Leaded copper	1079	954	0.323	8.94	0.0000098	10.5	99	222
Selenium copper	1070	1063	0.322	8.91	0.0000098	10.5	99	222

* Before precipitation heat treatment
** From 68 to 212°F.

points (liquidus and solidus), density, specific gravity, coefficient of linear thermal expansion, electrical resistivity, electrical conductivity, and thermal conductivity. Because these properties in general are essentially a function of alloy composition rather than temper or anneal, they are often classified as physical constants to distinguish them as a group from the mechanical properties that are controlled by mill treatment.

In Table 25-2 both liquidus and solidus melting points are listed. Usually when one melting point for an alloy is given it is commonly understood to mean the liquidus temperature.

Although the values for density or specific gravity of wrought copper alloys extend over a rather narrow range, they are significant as a precise basis for estimating the weights of material needed, since most mill products are priced by the pound.

The coefficient of linear thermal expansion varies with temperature and slightly with composition. Hidnert and Dickson[5, 6] have determined the coefficient for many of the alloys over a wide range of temperature.

The electrical resistivity and its reciprocal, conductivity, vary over a wide range with alloy composition. The temperature coefficient of resistivity is needed if the effect of temperature or its variations is of significance. The tabulated values are for metal in the annealed condition. In rolled or drawn tempers, the electrical conductivity is somewhat lower; Crampton, Burghoff, and Stacy[7] investigated this effect of cold work quantitatively in considerable detail. For copper-zinc, copper-tin, copper-phosphorus, copper-silicon, copper-aluminum, copper-nickel, copper-manganese, and other copper alloys, Smith and Palmer[8, 9, 10] determined both the electrical and thermal conductivity and arrived at a relation expressed by the approximate conversions in Table 25-3.

Values for modulus of elasticity in tension and modulus of rigidity are listed in Table 25-4. The effect of alloying elements on these properties is made evident to some degree. Poisson's ratio, sometimes included in tabulations of this type, is approximately 0.33 for wrought copper alloys.

The mechanical properties in Tables 25-5 to 25-10, inclusive, are those of most importance to engineers who need the data for structural design or for use as an approach to the formulation of specification requirements. Depending on the alloy and form, requirements are usually confined to tensile strength, yield strength, elongation, hardness, and grain size. In listing typical values, reasonable approximations suitable for general engineering use have been tabulated. Due to manufacturing limitations and commercial variations in composition, they should not be used directly for specification requirements; instead, reference should be made to the applicable ASTM specifications.

The basic mill forms usually available for the different alloys are

TABLE 25-3. APPROXIMATE CONVERSION OF THERMAL AND ELECTRICAL CONDUCTIVITIES OF COPPER-BASE ALLOYS AT 20°C (68°F)

Electrical Conductivity, Per Cent IACS at 20°C	Thermal Conductivity, Cal. per Sq Cm per Cm per Sec. per Deg. C at 20°C									
	0	1	2	3	4	5	6	7	8	9
0	0.018	0.028	0.038	0.047	0.057	0.067	0.077	0.086	0.096	0.106
10	0.116	0.126	0.136	0.146	0.156	0.166	0.176	0.186	0.195	0.205
20	0.215	0.225	0.235	0.245	0.255	0.265	0.275	0.285	0.294	0.304
30	0.314	0.324	0.334	0.343	0.353	0.363	0.373	0.382	0.392	0.402
40	0.411	0.421	0.431	0.440	0.450	0.460	0.470	0.479	0.489	0.499
50	0.508	0.518	0.528	0.537	0.547	0.556	0.565	0.574	0.584	0.593
60	0.602	0.611	0.620	0.629	0.638	0.647	0.656	0.665	0.674	0.682
70	0.691	0.699	0.708	0.716	0.724	0.733	0.741	0.749	0.757	0.766
80	0.774	0.782	0.790	0.798	0.806	0.814	0.821	0.829	0.837	0.845
90	0.852	0.860	0.867	0.875	0.882	0.890	0.897	0.905	0.912	0.920
100	0.927	0.934	0.941	0.949	0.956	—	—	—	—	—

Conversion Factors:

Thermal Conductivity, Btu/ft^2/in/sec/°F = Cal/cm^2/cm/sec/°C × 0.8064
Btu/ft^2/in/hr/°F = Cal/cm^2/cm/sec/°C × 2903.
Btu/ft^2/ft/hr/°F = Cal/cm^2/cm/sec/°C × 241.9

TABLE 25-4. MODULI OF ELASTICITY AND RIGIDITY

(Typical Values)

Name	Modulus of Elasticity in Tension, psi	Modulus of Rigidity, psi
Brasses—Nonleaded		
Gilding, 95%	17,000,000	6,400,000
Commercial bronze, 90%	17,000,000	6,400,000
Red brass, 85%	17,000,000	6,400,000
Low brass, 80%	16,000,000	6,000,000
Cartridge brass, 70%	16,000,000	6,000,000
Yellow brass, 66%	15,000,000	5,600,000
Yellow brass, 63%	15,000,000	5,600,000
Muntz metal	15,000,000	5,600,000
Leaded Brasses		
Leaded commercial bronze	17,000,000	6,400,000
Leaded tube brass	15,000,000	5,600,000
High-leaded tube brass	15,000,000	5,600,000
Low-leaded brass	15,000,000	5,600,000
Medium-leaded brass	15,000,000	5,600,000
High-leaded brass	15,000,000	5,600,000
Free-cutting brass	14,000,000	5,300,000
Leaded Muntz metal	15,000,000	5,600,000
Free-cutting Muntz metal	15,000,000	5,600,000
Forging brass	15,000,000	5,600,000
Architectural bronze	14,000,000	5,300,000
Tin and Aluminum Brasses		
Inhibited admiralty	16,000,000	6,000,000
Naval brass	15,000,000	5,600,000
Leaded naval brass	15,000,000	5,600,000
Manganese bronze, (A)	15,000,000	5,600,000
Aluminum brass	16,000,000	6,000,000
Phosphor Bronzes		
Phosphor bronze, 5% (A)	16,000,000	6,000,000
Phosphor bronze, 8% (C)	16,000,000	6,000,000
Phosphor bronze, 10% (D)	16,000,000	6,000,000
Phosphor bronze, 1.25% (E)	17,000,000	6,400,000
Leaded phosphor bronze	16,000,000	6,000,000
Free-cutting phosphor bronze	15,000,000	5,600,000
Cupronickels		
Cupronickel, 10%	18,000,000	6,800,000
Cupronickel, 30%	22,000,000	8,200,000
Nickel Silvers		
Nickel silver, 65-18	18,000,000	6,800,000
Nickel silver, 55-18	18,000,000	6,800,000
Nickel silver, 65-12	18,000,000	6,800,000
Nickel silver, 65-10	17,500,000	6,500,000
Silicon Bronzes (Copper-Silicon Alloys)		
High-silicon bronze (A)	15,000,000	5,600,000
Low-silicon bronze (B)	17,000,000	6,400,000

TABLE 25-4. MODULI OF ELASTICITY AND RIGIDITY (Cont'd)

Name	Modulus of Elasticity in Tension, psi	Modulus of Rigidity, psi
Aluminum Bronzes		
Aluminum bronze, 5%	17,000,000	6,400,000
Aluminum bronze, 8%	17,000,000	6,400,000
Aluminum bronze, (D)	17,500,000	6,500,000
Aluminum bronze, (E)	17,000,000	6,400,000
Aluminum-silicon bronze	16,000,000	6,000,000
Other Copper Alloys		
Cadmium bronze	17,000,000	6,400,000
Chromium copper*	19,000,000	7,200,000
Beryllium copper*	19,000,000	7,200,000
Leaded copper	17,000,000	6,400,000
Selenium copper	17,000,000	6,400,000

* Heat treated.

indicated in Table 25-1. Strip is material up to 0.188 inch thick and up to 20 inches wide; sheet is material up to 0.188 inch thick and over 20 inches wide; bar is material over 0.188 inch thick and up to 12 inches wide; and plate is material over 0.188 inch thick and over 12 inches wide.

For the alloy list as a whole, annealed tempers include soft anneal, light anneal, and a group of anneals designated according to nominal grain size in millimeters: 0.100, 0.070, 0.050, 0.035, 0.025, and 0.015. Rolled or drawn tempers include eighth hard, quarter hard, half hard, hard, extra hard, spring, extra spring, drawn—general purpose, hard drawn, and light drawn. Hot-finished tempers include as-hot-rolled and as-extruded. The tables for mechanical properties include the tempers commonly used, and sizes for the different mill forms have been selected as representative.

Tensile strength is the basic mechanical property in use for mill products, and yield strength at 0.5 per cent extension or elongation under load has been generally accepted for copper alloys. Smith and Van Wagner[11] are among those who have published data for other points on the stress-strain diagrams for some of the copper alloys. The reduction of area in the tension test is an indication of cold workability and although it is not made a specification requirement, it is of considerable interest and is frequently determined. Within limits depending on composition and temper, the shear strength bears some relation to tensile strength, although precise conversion factors have not been established. Within limits, Rockwell hardness can be correlated with grain size and tensile strength, and when properly applied it provides a rapid and inexpensive means for checking the approximate mechanical properties.

Endurance strength, determined by fatigue tests on rod and strip, is

Table 25-5. Mechanical Properties of Strip Metal
(Typical Values for Strip 0.040 inch Thick)

Temper	Tensile Strength, psi	Yield Strength (0.5% Extension Under Load), psi	Elongation in 2 in., per cent	Rockwell Hardness F	Rockwell Hardness B	Rockwell Hardness 30T	Shear Strength, psi
Gilding, 95%							
0.050 mm anneal	34,000	10,000	45	46	—	—	—
0.035 mm anneal	35,000	11,000	45	52	—	4	28,000
0.015 mm anneal	38,000	14,000	42	60	—	15	30,000
Quarter hard	42,000	32,000	25	—	38	44	32,000
Half hard	48,000	40,000	12	—	52	54	34,000
Hard	56,000	50,000	5	—	64	60	37,000
Extra hard	61,000	55,000	4	—	70	64	39,000
Spring	64,000	58,000	4	—	73	66	40,000
Commercial bronze, 90%							
0.050 mm anneal	37,000	10,000	45	53	—	6	28,000
0.035 mm anneal	38,000	12,000	45	57	—	12	30,000
0.025 mm anneal	39,000	14,000	44	60	—	16	31,000
0.015 mm anneal	41,000	15,000	42	65	—	26	32,000
Quarter hard	45,000	35,000	25	—	42	44	33,000
Half hard	52,000	45,000	11	—	58	56	35,000
Hard	61,000	54,000	5	—	70	63	38,000
Extra hard	67,000	58,000	4	—	75	67	40,000
Spring	72,000	62,000	3	—	78	69	42,000
As hot rolled	39,000	14,000	44	60	—	—	31,000
Red brass, 85%							
0.070 mm anneal	39,000	10,000	48	56	—	10	31,000
0.050 mm anneal	40,000	12,000	47	59	—	14	31,000
0.035 mm anneal	41,000	14,000	46	63	—	22	31,000
0.025 mm anneal	43,000	16,000	44	66	—	28	32,000
0.015 mm anneal	45,000	18,000	42	71	—	38	33,000
Quarter hard	50,000	39,000	25	—	55	54	35,000
Half hard	57,000	49,000	12	—	65	60	37,000
Hard	70,000	57,000	5	—	77	68	42,000
Extra hard	78,000	61,000	4	—	83	72	44,000
Spring	84,000	63,000	3	—	86	74	46,000

TABLE 25-5. MECHANICAL PROPERTIES OF STRIP METAL (Cont'd)

Temper	Tensile Strength, psi	Yield Strength (0.5% Extension Under Load), psi	Elongation in 2 in., per cent	Rockwell Hardness F	Rockwell Hardness B	Rockwell Hardness 30T	Shear Strength, psi
Low brass, 80%							
0.070 mm anneal	42,000	12,000	52	57	—	8	—
0.050 mm anneal	44,000	14,000	50	61	—	16	32,000
0.035 mm anneal	46,000	15,000	48	66	—	28	—
0.025 mm anneal	48,000	17,000	47	69	—	32	—
0.015 mm anneal	50,000	20,000	46	75	—	42	33,000
Quarter hard	53,000	40,000	30	—	55	54	36,000
Half hard	61,000	50,000	18	—	70	64	39,000
Hard	74,000	59,000	7	—	82	71	43,000
Spring	91,000	65,000	3	—	91	77	48,000
Cartridge brass, 70%							
0.100 mm anneal	44,000	11,000	66	54	—	11	—
0.070 mm anneal	46,000	14,000	65	58	—	15	32,000
0.050 mm anneal	47,000	15,000	62	64	—	26	—
0.035 mm anneal	49,000	17,000	57	68	—	31	34,000
0.025 mm anneal	51,000	19,000	55	72	—	36	—
0.015 mm anneal	53,000	22,000	54	78	—	43	35,000
Quarter hard	54,000	40,000	43	—	55	54	36,000
Half hard	62,000	52,000	23	—	70	65	40,000
Hard	76,000	63,000	8	—	82	73	44,000
Extra hard	86,000	65,000	5	—	88	76	46,000
Spring	94,000	65,000	3	—	91	77	48,000
Yellow brass, 66%							
0.070 mm anneal	46,000	14,000	65	58	—	15	32,000
0.050 mm anneal	47,000	15,000	62	64	—	26	—
0.035 mm anneal	49,000	17,000	57	68	—	31	34,000
0.025 mm anneal	51,000	19,000	55	72	—	36	—
0.015 mm anneal	53,000	22,000	54	78	—	43	—
Quarter hard	54,000	40,000	43	—	55	54	36,000
Half hard	61,000	50,000	23	—	70	65	40.000
Hard	74,000	60,000	8	—	80	70	43,000
Extra hard	85,000	62,000	5	—	87	74	45.000
Spring	91,000	62,000	3	—	90	76	47,000

TABLE 25-5. MECHANICAL PROPERTIES OF STRIP METAL (Cont'd)

Temper	Tensile Strength, psi	Yield Strength (0.5% Extension Under Load), psi	Elongation in 2 in., per cent	Rockwell Hardness F	Rockwell Hardness B	Rockwell Hardness 30T	Shear Strength, psi
Muntz metal							
Soft anneal	54,000	21,000	45	80	—	46	40,000
As hot rolled	54,000	21,000	45	85	—	49	40,000
Eighth hard	60,000	35,000	30	—	55	54	42,000
Half hard	70,000	50,000	10	—	75	67	44,000
Low-leaded brass							
0.070 mm anneal	46,000	14,000	65	58	—	15	32,000
0.050 mm anneal	47,000	15,000	62	64	—	26	—
0.035 mm anneal	49,000	17,000	57	68	—	31	34,000
0.025 mm anneal	51,000	19,000	55	72	—	36	—
Quarter hard	54,000	40,000	43	—	55	54	36,000
Half hard	61,000	50,000	23	—	70	65	40,000
Hard	74,000	60,000	8	—	80	69	43,000
Medium-leaded brass							
0.050 mm anneal	47,000	15,000	60	64	—	26	—
0.035 mm anneal	49,000	17,000	54	68	—	31	34,000
0.025 mm anneal	51,000	19,000	53	72	—	36	—
Quarter hard	54,000	40,000	41	—	55	54	36,000
Half hard	61,000	50,000	21	—	70	65	40,000
Hard	74,000	60,000	7	—	80	69	43,000
High-leaded brass							
0.035 mm anneal	49,000	17,000	52	68	—	31	34,000
Quarter hard	54,000	40,000	38	—	55	54	36,000
Half hard	61,000	50,000	20	—	70	65	40,000
Hard	74,000	60,000	7	—	80	69	43,000
Extra hard	85,000	62,000	5	—	87	74	45,000
Naval brass							
Light anneal	62,000	30,000	40	—	60	57	41,000
Quarter hard	70,000	58,000	17	—	75	68	43,000

TABLE 25-5. MECHANICAL PROPERTIES OF STRIP METAL (Cont'd)

Temper	Tensile Strength, psi	Yield Strength (0.5% Extension Under Load), psi	Elongation in 2 in., per cent	Rockwell Hardness F	Rockwell Hardness B	Rockwell Hardness 30T	Shear Strength, psi
Phosphor bronze, 5% (A)							
Soft	48,000	20,000	50	—	28	37	37,000
Half hard	68,000	55,000	28	—	78	69	47,000
Hard	81,000	75,000	10	—	87	75	54,000
Extra hard	92,000	80,000	6	—	93	78	60,000
Spring	100,000	80,000	4	—	95	79	—
Phosphor bronze, 8% (C)							
Soft	60,000	24,000	65	—	50	53	44,000
Half hard	76,000	55,000	32	—	84	73	50,000
Hard	93,000	72,000	10	—	93	78	60,000
Extra hard	106,000	80,000	4	—	96	80	65,000
Spring	112,000	—	3	—	98	81	—
Phosphor bronze, 10% (D)							
0.035 mm anneal	66,000	28,000	68	—	55	—	46,000
Half hard	83,000	—	32	—	92	—	—
Hard	100,000	70,000	13	—	97	—	—
Extra hard	115,000	—	7	—	100	—	—
Spring	122,000	—	4	—	101	—	—
Phosphor bronze, 1.25% (E)							
0.025 mm anneal	40,000	14,000	48	60	—	—	30,000
Half hard	55,000	—	16	—	64	60	—
Hard	65,000	50,000	8	—	75	67	—
Spring	75,000	—	4	—	79	70	—
Leaded phosphor bronze							
Soft	48,000	20,000	40	—	28	37	37,000
Half hard	68,000	55,000	24	—	78	69	47,000
Hard	81,000	75,000	8	—	87	75	54,000
Extra hard	92,000	80,000	5	—	93	78	60,000
Spring	100,000	80,000	3	—	95	79	—

TABLE 25-5. MECHANICAL PROPERTIES OF STRIP METAL (Cont'd)

Temper	Tensile Strength, psi	Yield Strength (0.5% Extension Under Load), psi	Elongation in 2 in., per cent	Rockwell Hardness F	Rockwell Hardness B	Rockwell Hardness 30T	Shear Strength, psi
Nickel silver, 65-18							
0.035 mm anneal	58,000	25,000	40	85	40	—	44,000
0.015 mm anneal	60,000	30,000	32	90	55	—	—
Quarter hard	65,000	50,000	20	—	73	65	—
Half hard	74,000	62,000	8	—	83	72	—
Hard	85,000	74,000	3	—	87	75	55,000
Nickel silver, 55-18							
0.035 mm anneal	60,000	27,000	40	90	55	—	45,000
Hard	100,000	85,000	3	—	91	77	65,000
Extra hard	108,000	90,000	2.5	—	96	80	—
Spring	115,000	—	2.5	—	99	81	—
Nickel silver, 65-12							
0.035 mm anneal	56,000	21,000	42	78	37	38	41,000
0.015 mm anneal	61,000	28,000	35	88	55	51	42,000
Quarter hard	65,000	45,000	23	—	70	63	44,000
Half hard	73,000	60,000	11	—	80	70	47,000
Hard	85,000	75,000	4	—	89	75	52,000
Extra hard	93,000	79,000	2	—	92	77	56,000
Nickel silver, 65-10							
0.035 mm anneal	53,000	20,000	43	76	35	38	41,000
0.015 mm anneal	60,000	28,000	36	85	52	51	43,000
Quarter hard	65,000	45,000	25	—	70	63	45,000
Half hard	73,000	60,000	12	—	80	70	50,000
Hard	86,000	75,000	4	—	89	76	55,000
Extra hard	95,000	76,000	3	—	92	78	59,000

TABLE 25-5. MECHANICAL PROPERTIES OF STRIP METAL (Cont'd)

Temper	Tensile Strength, psi	Yield Strength (0.5% Extension Under Load), psi	Elongation in 2 in., per cent	Rockwell Hardness F	Rockwell Hardness B	Rockwell Hardness 30T	Shear Strength, psi
High-silicon bronze, (A)							
0.070 mm anneal	56,000	21,000	63	76	40	—	42,000
0.035 mm anneal	60,000	25,000	60	85	62	—	43,000
Quarter hard	68,000	35,000	30	—	75	67	47,000
Half hard	78,000	45,000	17	—	87	75	50,000
Hard	94,000	58,000	8	—	93	78	57,000
Extra hard	104,000	60,000	6	—	96	80	60,000
Spring	110,000	62,000	4	—	97	81	63,000
Low-silicon bronze, (B)							
0.070 mm anneal	42,000	15,000	46	50	—	—	30,000
0.040 mm anneal	45,000	18,000	40	62	—	—	32,000
Half hard	52,000	30,000	15	—	56	—	—
Hard	65,000	50,000	8	—	68	—	42,000
Aluminum Bronze, 5%							
Soft	55,000	22,000	65	—	35	—	40,000
Hard	92,000	65,000	7	—	92	—	56,000
Aluminum bronze, 8%							
Soft	65,000	25,000	60	—	50	—	45,000
Hard	105,000	65,000	7	—	96	—	60,000
Beryllium copper							
A	69,000	35,000	35	—	62	57	52,000
¼ H	82,000	62,000	10	—	79	69	—
½ H	92,000	70,000	5	—	92	77	67,000
H	110,000	—	2	—	99	81	—
					C	30N	
AT	175,000	90,000	3		37	58	95,000
¼ HT	185,000	—	—		39	60	—
½ HT	195,000	95,000	2		41	62	100,000
HT	200,000	—	—		42	63	—

TABLE 25-6. MECHANICAL PROPERTIES OF ROD
(Typical Values)

Size of Section, inches	Temper	Tensile Strength, psi	Yield Strength, (0.5% Extension Under Load), psi	Elongation in 2 inches, per cent	Rockwell Hardness			Shear Strength, psi	Reduction of Area, %
					F	B	30T		
Commercial bronze, 90%									
0.500	0.035 mm anneal	40,000	14,000	50	55	—	—	32,000	—
	Eighth hard	45,000	35,000	25	—	42	—	33,000	—
Cartridge brass, 70%									
1.0	0.050 mm anneal	48,000	16,000	65	65	—	—	34,000	75
	Eighth hard (6%)	55,000	40,000	48	—	60	—	36,000	70
	Half hard (20%)	70,000	52,000	30	—	80	—	42,000	68
Yellow brass, 63%									
1.0	0.050 mm anneal	48,000	16,000	65	65	—	—	34,000	75
	Eighth hard (6%)	55,000	40,000	48	—	55	—	36,000	70
Leaded commercial bronze									
1.0	0.050 mm anneal	37,000	12,000	45	55	—	—	24,000	70
0.250	Half hard (37%)	60,000	55,000	10	—	65	—	32,000	—
0.500	Half hard (25%)	55,000	50,000	14	—	61	—	31,000	—
1.0	Half hard (20%)	52,000	45,000	18	—	58	—	30,000	60
Medium-leaded brass									
1.0	0.025 mm anneal	50,000	19,000	60	70	—	—	34,000	—
	Quarter hard (10%)	55,000	42,000	40	—	60	—	36,000	—
High-leaded brass									
1.0	Half hard (20%)	58,000	45,000	25	—	75	—	35,000	50
Free-cutting brass									
1.0	Soft anneal	49,000	18,000	53	68	—	—	30,000	58
0.250	Half hard (25%)	68,000	52,000	18	—	80	—	38,000	48
1.0	Half hard (20%)	58,000	45,000	25	—	78	—	34,000	50
2.0	Half hard (15%)	55,000	44,000	32	—	75	—	32,000	52

TABLE 25-6. MECHANICAL PROPERTIES OF ROD (Cont'd)

Size of Section, inches	Temper	Tensile Strength, psi	Yield Strength, (0.5% Extension Under Load), psi	Elongation in 2 inches, per cent	Rockwell Hardness F	Rockwell Hardness B	Rockwell Hardness 30T	Shear Strength, psi	Reduction of Area, %
Forging brass									
1.0	As extruded	52,000	20,000	45	78	—	—	30,000	65
Naval brass									
0.250	Soft anneal	58,000	27,000	45	—	56	—	40,000	60
	Light anneal	63,000	30,000	40	—	60	—	42,000	55
	Quarter hard (10%)	70,000	48,000	25	—	80	—	43,000	50
	Half hard (20%)	80,000	57,000	20	—	85	—	45,000	45
1.0	Soft anneal	57,000	25,000	47	—	55	—	40,000	60
	Light anneal	63,000	30,000	40	—	60	—	42,000	55
	Quarter hard (8%)	69,000	46,000	27	—	78	—	43,000	50
	Half hard (20%)	75,000	53,000	20	—	82	—	44,000	45
2.0	Soft anneal	56,000	25,000	47	—	55	—	40,000	60
	Light anneal	62,000	28,000	43	—	60	—	42,000	55
	Quarter hard (8%)	67,000	40,000	35	—	75	—	43,000	50
Leaded naval brass									
1.0	Soft anneal	57,000	25,000	40	—	55	—	36,000	—
	Quarter hard (8%)	69,000	46,000	20	—	78	—	39,000	—
	Half hard (20%)	75,000	53,000	15	—	82	—	40,000	—
Manganese bronze, (A)									
1.0	Soft anneal	65,000	30,000	33	—	65	—	42,000	—
	Quarter hard (10%)	77,000	45,000	23	—	83	—	47,000	—
	Half hard (20%)	84,000	60,000	19	—	90	—	48,000	—
2.0	Quarter hard (10%)	72,000	42,000	27	—	77	—	44,000	—
Phosphor bronze, 5% (A)									
0.500	Half hard (20%)	75,000	65,000	25	—	80	—	52,000	—
1.0	Half hard (20%)	70,000	58,000	25	—	78	—	50,000	75

TABLE 25-6. MECHANICAL PROPERTIES OF ROD (Cont'd)

Size of Section, inches	Temper	Tensile Strength, psi	Yield Strength, (0.5% Extension Under Load), psi	Elongation in 2 inches, per cent	Rockwell Hardness			Shear Strength, psi	Reduction of Area, %
					F	B	30T		
Phosphor bronze, 8% (C)									
0.500	Half hard (20%)	80,000	65,000	33	—	85	—	54,000	77
Leaded phosphor bronze									
1.0	Half hard (20%)	65,000	55,000	25	—	75	—	40,000	—
Free-cutting phosphor bronze									
1.0	Half hard (20%)	60,000	45,000	20	—	75	—	35,000	—
Cupronickel, 30%									
1.0	Half hard (20%)	75,000	70,000	15	—	80	—	42,000	—
Nickel silver, 65-18									
0.500	0.035 mm anneal	56,000	25,000	42	—	—	—	43,000	—
	Half hard (20%)	70,000	60,000	20	—	78	—	—	60
Nickel silver, 55-18									
1.0	Half hard (20%)	80,000	60,000	20	—	85	—	53,000	—
High-silicon bronze, (A)									
1.0	0.050 mm anneal	58,000	22,000	60	—	60	—	43,000	80
	Half hard (20%)	78,000	45,000	35	—	85	—	52,000	65
	Hard (36%)	92,000	55,000	22	—	90	—	58,000	62
	Extra hard (50%)	108,000	60,000	13	—	95	—	62,000	60
Low-silicon bronze, (B)									
1.0	0.035 mm anneal	40,000	15,000	50	55	—	—	29,000	87
	Hard (36%)	70,000	55,000	15	—	80	—	45,000	—
	Extra hard (50%)	90,000	67,000	12	—	90	—	50,000	—

TABLE 25-6. MECHANICAL PROPERTIES OF ROD (Cont'd)

Size of Section, inches	Temper	Tensile Strength, psi	Yield Strength, (0.5% Extension Under Load), psi	Elongation in 2 inches, per cent	Rockwell Hardness			Shear Strength, psi	Reduction of Area, %
					F	B	C		
Aluminum bronze, 5%									
1.0	Soft	55,000	22,000	65	—	35	—	38,000	—
Aluminum bronze, 8%									
1.0	Soft	65,000	25,000	65	—	50	—	45,000	70
	Hard	80,000	50,000	30	—	—	—	53,000	—
Aluminum bronze, (E)									
1.0	Hard	105,000	60,000	12	—	105	—	—	—
Aluminum-silicon bronze									
1.0	Soft	95,000	53,000	25	—	95	—	48,000	33
Chromium copper									
1.0	A	35,000	15,000	40	50	—	—	—	—
	H	62,000	57,000	20	—	70	—	—	—
	AT	63,000	45,000	25	—	65	—	—	—
	HT	72,000	61,000	25	—	77	—	—	53
Beryllium copper									
1.0	A	73,000	35,000	40	—	65	—	54,000	55
	H	105,000	80,000	15	—	97	—	75,000	25
	AT	175,000	90,000	6	—	—	37	95,000	5
	HT	195,000	95,000	4	—	—	41	100,000	3
Leaded copper									
1.0	Hard	45,000	40,000	12	—	50	—	—	—
Selenium copper									
1.0	Hard	45,000	40,000	12	—	50	—	—	—

TABLE 25-7. MECHANICAL PROPERTIES OF WIRE

(Typical Values for 0.080 Inch Diameter)

Temper	Tensile Strength, psi	Yield Strength (0.5% Extension Under Load), psi	Elongation in 2 inches, per cent	Shear Strength, psi
Commercial bronze, 90%				
0.035 mm anneal	40,000		50	30,000
0.015 mm anneal	42,000		48	32,000
Eighth hard	44,000		27	33,000
Quarter hard	50,000		13	34,000
Half hard	60,000		6	37,000
Hard	74,000		4	42,000
Extra hard	83,000		3	
Spring	90,000		3	
Red brass, 85%				
0.035 mm anneal	41,000		48	31,000
0.025 mm anneal	43,000			32,000
0.015 mm anneal	45,000			33,000
Eighth hard	50,000		25	35,000
Quarter hard	59,000		11	38,000
Half hard	72,000		8	43,000
Hard	88,000		6	48,000
Spring	105,000			54,000
Low brass, 80%				
0.050 mm anneal	44,000		55	32,000
0.035 mm anneal	46,000		50	
0.015 mm anneal	50,000		47	33,000
Eighth hard	56,000		27	37,000
Quarter hard	68,000		12	42,000
Half hard	82,000		8	47,000
Hard	107,000		5	53,000
Extra hard	116,000		4	
Spring	125,000		3	60,000
Cartridge brass, 70%				
0.050 mm anneal	48,000		64	
0.035 mm anneal	50,000		60	34,000
0.025 mm anneal	52,000		58	
0.015 mm anneal	54,000		56	
Eighth hard	58,000		35	38,000
Quarter hard	70,000		20	
Extra hard	124,000		4	
Spring	130,000		3	60,000
Yellow brass				
0.035 mm anneal	50,000		60	34,000
Eighth hard	58,000		35	38,000
Quarter hard	70,000		20	42,000
Half hard	88,000		15	
Hard	110,000		8	55,000
Extra hard	120,000		4	
Spring	128,000		3	60,000
Medium-leaded brass				
0.025 mm anneal	50,000		60	34,000
Eighth hard	58,000		45	38,000
Half hard	88,000		15	46,000

TABLE 25-7. MECHANICAL PROPERTIES OF WIRE (Cont'd)

Temper	Tensile Strength, psi	Yield Strength (0.5% Extension Under Load), psi	Elongation in 2 inches, per cent	Shear Strength, psi
Phosphor bronze, 5% (A)				
0.035 mm anneal	50,000	20,000	58	
Quarter hard	68,000	60,000	24	
Half hard	85,000	80,000	8	
Hard	110,000		5	
Extra hard (75%)	130,000		3	
Spring (84%)	140,000		2	
Phosphor bronze, 8% (C)				
0.035 mm anneal	60,000	24,000	65	
Quarter hard	81,000			
Half hard	105,000			
Hard	130,000			
Extra hard	140,000			
Phosphor bronze, 10% (D)				
0.035 mm anneal	66,000		70	
Quarter hard	93,000			
Half hard	118,000			
Hard	147,000			
Nickel silver, 65-18				
0.035 mm anneal	58,000	25,000	45	
0.015 mm anneal	60,000	30,000	35	
Quarter hard	73,000	65,000	16	
Half hard	86,000	80,000	7	
Hard	103,000	90,000	3	
Nickel silver, 55-18				
0.035 mm anneal	60,000		40	
Spring (68%)	145,000		2	
Nickel silver, 65-10				
0.035 mm anneal	56,000		45	
0.015 mm anneal	63,000		35	
Eighth hard (10%)	65,000		25	
Quarter hard (20%)	72,000		10	
Half hard (37%)	85,000		7	
Hard (60%)	105,000		5	
Extra hard (75%)	120,000		3	
Spring (84%)	130,000		1	
High-silicon bronze, (A)				
0.035 mm anneal	60,000	25,000	60	43,000
Eighth hard	70,000	40,000	35	48,000
Quarter hard	80,000	48,000	20	52,000
Half hard	98,000	57,000	8	58,000
Hard	125,000	65,000	5	65,000
Spring (80%)	145,000	70,000	3	70,000
Low-silicon bronze, (B)				
Eighth hard	50,000	35,000	40	36,000
Quarter hard	57,000	45,000	25	40,000
Half hard	70,000	55,000	15	45,000
Hard	90,000	67,000	12	50,000
Extra hard	95,000	69,000	11	53,000

TABLE 25-7. MECHANICAL PROPERTIES OF WIRE (Cont'd)

Temper	Tensile Strength, psi	Yield Strength (0.5% Extension Under Load), psi	Elongation in 2 inches, per cent	Shear Strength, psi
Cadmium bronze				
Hard	90,000		1*	
Beryllium copper				
A	68,000			
¼ H	103,000			
½ H	123,000			
¾ H	143,000			
AT	175,000			
¼ HT	190,000			
½ HT	200,000			
¾ HT	210,000			

* Elongation in 10 inches.

listed in Table 25-11. Anderson, Smith, Swan, and Palmer[12, 13] tested rotating-beam rod specimens and Burghoff and Blank[14] and Gohn and Ellis[15] have investigated the fatigue properties of copper alloys in strip form.

The properties of copper alloys in compression have not had much attention, but since some of the alloys are used for some types of bearing applications, data are listed in Table 25-12.

Creep strength is one of the criteria for establishing allowable stress values at elevated temperatures. In Table 25-13 the values for red brass, Muntz metal, and Tobin Bronze were reported by Clark and White[16] from tests made at the University of Michigan, where the values for the remainder of the alloys in the table were determined for The American Brass Co. Burghoff and Blank[17] have investigated creep characteristics of some of the copper alloys at 150, 205, and 260°C (300, 400, and 500°F).

After reviewing the literature, Smith[18] summarized the mechanical properties of copper and its alloys at low temperatures as follows:

> "All wrought copper alloys are alike in that the effect of temperatures lower than normal is to improve all useful mechanical properties. Hardness, yield strength, and tensile strength show material improvement, and the ductility (particularly as shown by elongation) is better at the temperature of liquid air or below than at room temperatures. Impact properties are practically unaffected. The ductility of cold-worked alloys increases to a greater extent than does that of annealed material, and they are, therefore, the logical materials for stressed parts for low-temperature service. Castings of copper alloys show a small decrease in ductility at low temperatures."

Tables 25-14 and 25-15 are from his review.

Standard Specifications

In the field of materials, a standard specification may be defined as a published document that describes the required qualities of a commodity or a group of commodities in clear, concise language and engineering units, together with sampling and test methods for determining compliance with these prescribed requirements. Such documents are adopted voluntarily by industry and when applied to orders for material they become part of the business contract in commercial transactions.

For wrought copper alloys, the various standard specifications for mill products are of great value to both the producer and the consumer in providing a common terminology to facilitate the procurement of satisfactory material. As with many other commodities, the development of standard specifications for brass-mill products has been advancing at an accelerated pace for almost fifty years; and it is a continuing task. It might be thought that the most important attribute of standards would be stability. Yet their greatest value to industry as a buying instrument is in reflecting current ability to produce. Constant revision must, therefore, take place, and by the same token it is practically impossible to set forth in one document the manufacturing limitations of all producers. In other words, a specification can not become a seller's catalog.

Prior to the use of standards, the mill and the customer usually were obliged to negotiate painstakingly each item, often by trial-and-error methods based largely on experience or on the ability to duplicate samples. Explicit standards of quality have enabled all types of producers and consumers to avoid much of this detail.

Specifications for wrought copper alloys include brass, leaded brass, leaded red brass, cartridge brass, naval brass, manganese bronze, copper-nickel alloys, copper-nickel-zinc alloys, copper-silicon alloys, and copper-beryllium alloy in such mill forms as plate, sheet, strip, bullet-jacket cups, cartridge-case cups, rolled bar, drawn bar, drawn rod, drawn shapes, extruded shapes, piston-finish rod, shafting, and such seamless tubular products as general-purpose tubes, condenser tubes and ferrule stock, boiler tubes, pipe, and bright-annealed tube.

A typical copper-alloy specification covers such topics as scope, manufacture, chemical composition, physical or mechanical properties, sampling, methods of analysis and tests, dimensional tolerances, workmanship, marking, packing, retests, and rejection.

As far as possible, the stipulation of methods of manufacture is confined to those terms that will enable the consumer to obtain the proper kind and quality of material, and is not intended to dictate the mill proce-

Table 25-8. Mechanical Properties of Tube
(Typical Values)

Size of Section	Temper	Tensile Strength, psi	Yield Strength (0.5% Extension Under Load), psi	Elongation in 2 inches, per cent	Rockwell Hardness		
					F	B	30T
Commercial bronze, 90%							
1.0 inch O.D. by 0.065 inch	0.035 mm anneal	38,000	12,000	50	57	—	12
	Hard drawn (35%)	60,000	53,000	6	—	69	62
Red brass, 85%							
1.0 inch O.D. by 0.065 inch	0.050 mm anneal	40,000	12,000	55	60	—	15
	0.015 mm anneal	44,000	18,000	45	71	—	38
	Light drawn (15%)	50,000	40,000	30	—	55	54
	Hard drawn (35%)	70,000	58,000	8	—	77	68
¾ inch S.P.S.	0.015 mm anneal	44,000	18,000	45	71	—	—
Cartridge brass, 70%							
1.0 inch O.D. by 0.065 inch	0.050 mm anneal	47,000	15,000	65	64	—	26
	0.025 mm anneal	52,000	20,000	55	75	—	40
	Hard drawn (35%)	78,000	64,000	8	—	82	73
Muntz metal							
1.0 inch O.D. by 0.065 inch	Light anneal	56,000	23,000	50	82	—	47
	Hard drawn (30%)	74,000	55,000	10	—	80	—
Low-leaded tube brass							
1.0 inch O.D. by 0.065 inch	0.050 mm anneal	47,000	15,000	60	64	—	26
	0.025 mm anneal	52,000	20,000	50	75	—	37
	Hard drawn (35%)	75,000	60,000	7	—	80	69
High-leaded tube brass							
1.0 inch O.D. by 0.065 inch	0.025 mm anneal	52,000	20,000	50	75	—	36
	Hard drawn (35%)	75,000	60,000	7	—	80	69

TABLE 25-8. MECHANICAL PROPERTIES OF TUBE (Cont'd)

Size of Section	Temper	Tensile Strength, psi	Yield Strength (0.5% Extension Under Load), psi	Elongation in 2 inches, per cent	Rockwell Hardness F	Rockwell Hardness B	Rockwell Hardness 30T
Free-cutting Muntz metal							
1.5 inch O.D. by ⅛ inch	Light anneal	54,000	20,000	40	80	—	43
	Hard drawn (35%)	80,000	60,000	6	—	85	74
2 inch O.D. by ¼ inch	Hard drawn (25%)	70,000	45,000	10	—	75	67
Inhibited admiralty							
1.0 inch O.D. by 0.065 inch	0.025 mm anneal	53,000	22,000	65	75	—	37
Aluminum brass							
1.0 inch O.D. by 0.065 inch	0.025 mm anneal	60,000	27,000	55	77	—	—
Cupronickel, 10%							
1.0 inch O.D. by 0.065 inch	0.025 mm anneal	44,000	16,000	42	65	15	26
	Light drawn	60,000	57,000	10	100	72	70
Cupronickel, 30%							
1.0 inch O.D. by 0.065 inch	0.025 mm anneal	60,000	25,000	45	80	45	—
4.5 inch O.D. by 0.109 inch	0.035 mm anneal	54,000	—	45	77	36	—
High-silicon bronze, (A)							
1.0 inch O.D. by 0.065 inch	0.050 mm anneal	57,000	—	70	—	45	—
Low-silicon bronze, (B)							
1.0 inch O.D. by 0.065 inch	0.015 mm anneal	45,000	20,000	55	68	—	—
	Hard drawn (35%)	65,000	40,000	20	—	75	67
Aluminum bronze, 5%							
1.0 inch O.D. by 0.065 inch	0.025 mm anneal	60,000	27,000	55	77	—	—

Table 25-9. Mechanical Properties of Plate (Typical Values)

Thickness, inches	Temper	Tensile Strength, psi	Yield Strength (0.5% Extension Under Load), psi	Elongation in 2 inches, per cent	Rockwell Hardness F	Rockwell Hardness B	Rockwell Hardness 30T	Shear Strength, psi
Leaded Muntz metal								
1.0	As hot rolled	54,000	20,000	45	80	—	—	40,000
Inhibited admiralty								
1.0	As hot rolled	48,000	18,000	65	70	—	—	—
Naval brass								
¼	Soft annealed	58,000	25,000	49	—	56	55	40,000
	Light annealed	60,000	28,000	45	—	58	56	41,000
1.0	As hot rolled	55,000	25,000	50	—	55	55	40,000
Manganese bronze, (A)								
¼	Soft	65,000	30,000	30	—	65	—	42,000
Cupronickel, 10%								
1.0	Soft	42,000	15,000	40	—	15	—	—
Aluminum bronze, (D)								
1.0	As hot rolled	75,000	35,000	40	—	80	—	—
Aluminum bronze, (E)								
1.0	As hot rolled	95,000	40,000	15	—	95	—	—

TABLE 25-10. MECHANICAL PROPERTIES OF FORGINGS AS HOT-PRESSED (Typical Values)

Alloy	0.505-inch Diameter Test Section			
	Tensile Strength, psi	Yield Strength (0.5% Extension Under Load), psi	Elongation in 4 × D, per cent	Rockwell Hardness (Filed surface, ⅛ inch chord min.) B Scale
Forging brass	58,000	23,000	40	45
Naval brass	64,000	26,000	40	55
Leaded naval brass	62,000	24,000	40	55
Manganese bronze, (A)	72,000	34,000	33	69
High-silicon bronze, (A)	52,000	18,000	70	62
Aluminum-silicon bronze	83,000	41,000	35	77

TABLE 25-11. ENDURANCE STRENGTH

Form	Size of Section, inches	Temper	Tensile Strength, 1000 psi	Endurance Strength	
				Psi	Million Cycles
Commercial bronze, 90%					
Strip	0.040	Spring	72	21,000	15
Wire	0.080	Hard	74	23,000	100
Red brass, 85%					
Wire	0.080	Eighth hard	50	20,000*	300
Low brass, 80%					
Strip	0.040	Spring	91	24,000	20
Wire	0.080	Hard	107	23,000	100
		Spring	125	26,000	100
Cartridge brass, 70%					
Strip	0.040	0.100 mm anneal	44	13,000	100
		0.070 mm anneal	46	13,000	100
		0.035 mm anneal	49	14,000	100
		0.015 mm anneal	53	15,000	100
		Half hard	62	18,000	100
		Hard	76	21,000	100
		Spring	94	23,000	100
Wire	0.080	Spring	130	22,000	100
Rod	1.0	Half hard (20%)	70	22,000	50
Yellow brass, 66%					
Strip	0.040	0.070 mm anneal	46	12,000	100
		Hard	74	14,000	100
		Spring	91	20,000	100
Wire	0.080	Quarter hard	70	22,000*	300
Free-cutting brass					
Rod	2.0	Half hard (15%)	55	20,000**	100
				14,000**	300

* Rotating beam tests on rod.
** Independent rotating beam tests; diameter of test section, 0.350 in.

TABLE 25-11. ENDURANCE STRENGTH (Cont'd)

Form	Size of Section, inches	Temper	Tensile Strength, 1000 psi	Endurance Strength	
				Psi	Million Cycles
Tobin Bronze[a]					
Rod[b]	1.0	Hard (9.4%)	66	28,000	300
	0.5	Hard (11.5%)	70	24,000	300
Naval brass					
Rod[c]	1.0	Hard (11.5%)	70	15,000	300
		Hard (11.5%)	72	15,000	300
Phosphor bronze, 5% (A)					
Strip	0.040	Hard	81	25,000	100
		Spring	100	22,000	100
Wire	0.080	Hard	110	27,000	100
		Extra hard (75%)	130	30,000	100
Rod	0.5	Hard (30%)	70	29,000	300
Phosphor bronze, 8% (C)					
Strip	0.040	Hard	93	22,000	100
Rod	0.5	Half hard (15%)	66	30,000	300
		Hard (30%)	81	35,000	300
		Extra hard (50%)	110	30,000	300
Phosphor bronze, 1.25% (E)					
Wire	0.080	Hard (80%)	79	32,000	100
Rod	0.4	Hard (37%)	59	31,000	300
Nickel silver, 65-18					
Rod	0.5	Hard (21%)	73	23,000	300
High-silicon bronze, (A)					
Wire	0.080	Hard	125	29,000	100
		Spring (80%)	145	30,000	100
Rod	0.5	Soft	60	19,000	300
	0.4	Quarter hard (8%)[d]	67	31,000	300
	0.4	Half hard (20%)[e]	75	30,000	300
	0.5	Hard (39%)	97	33,000	300
Low-silicon bronze, (B)					
Wire	0.080	Hard	90	25,000	100
		Extra hard	95	28,000	100
Rod	0.5	Extra hard (72%)	88	30,000	300
Chromium copper					
Rod	0.5	HT	77	28,000	300
Beryllium copper					
Rod	0.5	HT	187	55,000	300

[a] Same chemical composition as naval brass.
[b] Hot rolled prior to cold work.
[c] Extruded prior to cold work.
[d] Ready-to-finish grain size, 0.035 mm.
[e] Ready-to-finish grain size, 0.065 mm.

TABLE 25-12. COMPRESSION TEST DATA

Name	Form	Temper	Tensile Strength, psi	Dimensions of Compression Sample, inches	Compressive Stress, psi at 0.10% Set	Compressive Stress, psi at 1.00% Set	Permanent Set Under 100,000 psi, per cent
Muntz metal	Rod	Soft	62,000	1.188 dia. by 2	18,300	28,700	20.7
Naval brass	Rod	—	67,000	1 dia. by 1	39,000	60,000	15.8
	Rod	—	59,000	1 dia. by 1	15,500	27,000	22.2
	Plate	Half hard	64,000	1 sq. by 1	40,000	52,000	17.6
Phosphor bronze, 5% (A)	Plate	Hard (37%)	—	1.128 dia. by 1	76,000	87,300	7.4
Phosphor bronze, 10% (D)	Plate	Quarter hard (11%)	70,000	1 sq. by 1	48,000	59,500	15.0
	Plate	Half hard (21%)	83,000	1 sq. by 1	73,000	83,500	6.1
Leaded phosphor bronze	Rod	Half hard (21%)	64,000	1 dia. by 1	47,500	63,800	23.7
	Plate	—	64,000	1 sq. by 1	58,800	69,300	18.1
Free-cutting phosphor bronze	Rod	Half hard (21%)	68,000	1 dia. by 1	49,500	64,000	23.9
High-silicon bronze, (A)	Plate	—	66,000	1 sq. by 1	28,000	—	16.4
	Plate	Half hard (18%)	80,000	1 sq. by 1	76,000	—	3.3
Beryllium copper	—	Cold worked	95,000	—	85,000	110,000	—
	—	Cold worked and heat treated	195,000	—	190,000	210,000	—

Table 25-13. Creep Strength

		Tensile Properties			
Name	Temperature of Test, °F	Tensile Strength, psi	Yield Strength (0.5% Extension Under Load), psi	Elongation in 2 inches, per cent	Creep Strength psi, 0.01% Extension per 1000 hours
Red brass, 85%	75	43,800	—	47.0	—
	400	38,525	—	—	8,800
	600	29,950	—	—	1,000
Cartridge brass, 70%	75	70,000	—	24.3	—
	400	65,550	—	—	12,700
	600	51,500	—	—	290
Muntz metal	75	55,350	—	51.0	—
	300	—	—	—	9,000
	400	45,750	—	—	2,000
Admiralty	75	68,500	—	35.0	—
	400	65,950	—	—	13,000
	600	55,800	—	—	1,000
	800	26,400	—	—	54
Tobin Bronze	75	62,750	—	46.0	—
	300	—	—	—	12,000
	400	45,875	—	—	3,500
*Cupronickel, 10%, annealed	Room	46,600	34,200	39.0	—
	600	—	—	—	6,000
**Cupronickel, 30%, cold drawn	85	64,700	48,300	37.0	—
	750	47,550	—	22.5	9,100
High-silicon bronze, (A), hot-rolled-and-annealed rod	85	66,000	19,650	56.2	—
	400	—	—	—	10,500
Aluminum bronze, (E)					
Extruded-and-drawn rod	85	121,300	81,500	15.5	—
	350	116,000	—	14.8	—
	500	—	—	—	12,000
Hot rolled plate	80	80,500	35,500	14	—
	600	70,200	—	16	12,000
	700	58,200	—	12	6,000
Chromium copper, heat treated	85	75,200	67,800	23.5	—
	650	—	—	—	8,500

* Tests made on specimens containing 0.89% iron.

** One specimen from this same bar annealed at 700°C and tested at 750°F at 9,000 lb per sq inch showed a creep rate of 0.0004% in 1,000 hours.

TABLE 25-14. PROPERTIES OF BRASS AT LOW TEMPERATURES*

Material	Temperature of Test Deg. C	Temperature of Test Deg. F	Yield Point (Amsler Recorder), psi	Tensile Strength, psi	Elongation in 50 mm, per cent	Reduction of Area, per cent	Impact Resistance, kg-m per sq cm (10 by 8 by 100-mm Specimen, 45-deg. Sharp V Notch)
Brass, 33% Zn, annealed 2 hr at 550°C	23	73	39,300	57,000	50.4	72.0	14.4
	−78	−110	43,700	61,200	49.8	76.6	16.9
	−183	−295	57,200	76,400	50.8	70.7	14.1
Brass, 33% Zn, cold worked 40% reduction	23	73	84,600	85,400	6.3	66.5	8.1
	−78	−110	91,800	92,500	7.8	71.5	9.2
	−183	−295	101,700	102,900	10.1	66.5	9.4
Brass, 40% Zn, annealed 2 hr at 550°C	20	68	19,900	57,600	51.3	75.5	8.6
	−78	−110	22,500	61,200	53.0	74.6	8.6
	−183	−295	28,500	75,800	55.3	71.0	8.3
Brass, 40% Zn, cold worked 25% reduction	21	70	56,900	79,700	19.8	65.5	5.1
	−78	−110	59,900	83,000	21.0	67.7	5.3
	−183	−295	80,100	98,400	24.4	64.1	5.3
Leaded brass, 40% Zn, 1.3% Pb, annealed 2 hr at 550°C	20	68	20,600	52,800	50.2	62.5	4.4
	−78	−110	24,600	54,600	49.8	64.0	4.9
	−183	−295	28,900	69,000	50.6	62.1	4.6
Leaded brass, 40% Zn, 1.3% Pb, cold worked 12% reduction	22	72	45,800	63,800	28.2	57.0	2.2
	−78	−110	54,100	70,400	27.0	59.0	2.5
	−183	−295	69,900	86,600	30.8	57.0	2.2

* Tests on brass by Broniewski and Wesolowski, using test specimen 5 mm in diameter. A few apparent misprints have been corrected by Smith.[18]

TABLE 25-15. IMPACT TESTS ON SOME ANNEALED COPPER ALLOYS

	Admiralty Brass	Tobin Bronze	Cupronickel, 30%	High-silicon Bronze, (A)
Copper, per cent	70.57	60.25	69.27	95.75
Zinc, per cent	28.44	38.91	0.62	—
Lead, per cent	0.01	0.01	—	—
Tin, per cent	0.95	0.75	—	—
Iron, per cent	0.03	0.08	—	0.17
Nickel, per cent	—	—	29.54	—
Silicon, per cent	—	—	—	3.05
Manganese, per cent	—	—	0.57	0.98
Yield strength, psi, 0.5 per cent elongation under load	13,300	35,000	34,200	29,900
Tensile strength, psi	46,500	64,600	57,600	62,400
Elongation, per cent (2-inch gage length, 0.7-inch dia.)	83.5	41.0	53.5	65.5
Rockwell hardness	"F" 64	"B" 61	"B" 55	"B" 54
Charpy Impact Resistance, Foot-pounds				
−115°C (−175°F)	59.2	16.9	60.0	64.5
−80°C (−110°F)	61.5	17.9	58.7	69.2
−50°C (−60°F)	58.9	18.1	59.4	73.1
−30°C (−25°F)	60.8	18.3	59.4	74.6
−18°C (0°F)	58.8	17.6	60.0	80.1
3°C (38°F)	60.6	16.1	63.9	73.3
20°C (70°F)	60.8	16.1	66.3	66.4
65°C (150°F)	51.0	14.7	53.0	59.8
120°C (250°F)	47.8	13.6	52.5	55.0
205°C (400°F)	45.2	11.7	50.2	50.2

Tensile tests at room temperatures on specimens 0.7 in. in diameter. Impact tests made by Battelle Memorial Institute in 1936 for The American Brass Company. All alloys were tested in annealed condition. Standard Charpy specimens (keyhole notch) cut from ¾-in. diameter rods. 120 ft-lb Amsler machine used. Specimens tested in standard time of 5 sec after removal from bath at stated temperature. Specimens at −115°C were frozen in ether with liquid air and allowed to heat to testing temperature. All others in bath 15 min at testing temperature. Figures are average of three tests. All Charpy specimens were unfractured except those of Tobin Bronze.

dures necessary to meet composition, physical, or other requirements. Before the development of standard requirements for physical properties and laboratory tests for compliance, it was often necessary to write manufacturing requirements in considerably more detail.

Requirements for chemical composition are two-fold: (a) limits for alloying elements, and (b) permissible maximum values for impurities. Limits for alloying elements serve to identify the material and control its quality for the purpose intended. Impurity allowances recognize the impossibility in commercial practice of totally excluding certain elements, and at the same time stipulate a tolerance that will protect the user from harmful amounts of such elements.

Mechanical or physical properties usually include tensile, hardness, or grain-size requirements. These control the designated condition or temper of the alloy and may have a double purpose: (a) to assist the fabricator in obtaining material of closely uniform temper for severe and precise fabricating operations, and (b) to assure the engineer of strength or other properties essential to the safe and proper functioning of structures, devices, or equipment.

Published standards now cover so many materials that it is common practice to include in one document several mill forms and the various tempers for a group of related alloys. The more general requirements, which usually include nearly all except composition and physical properties, may be segregated into companion documents.

In the United States, the promulgation of standards for materials is carried on principally by the American Society for Testing Materials through its technical committees, on which representatives of producers, consumers, and a general-interest group serve. In the technical committees the various proposals for new standards or revisions of existing standards receive thorough consideration in the form of discussion and correspondence in order to arrive at requirements that will be mutually satisfactory to all. The standards are issued with a fixed designation consisting of a significant letter, which in the case of copper-base alloys is "B" for nonferrous materials, plus a serial number, and to this are added two digits indicating the year of latest revision plus in some cases the letter "T" to indicate publication as a tentative specification prior to adoption as standard (for example B 122-52T). Under its standardization procedure, ASTM issues its standards first as "tentative" to elicit criticism and comment.

In the field of materials the American Standards Association endorses certain ASTM standards with a covering ASA designation. As far as possible the American Society of Mechanical Engineers adopts ASTM specifications for ASME use. The Society of Automotive Engineers bases SAE specifications on ASTM requirements. Federal and Military specifications generally reflect ASTM practice and are issued for use in Government purchasing.

For information on detailed requirements for wrought copper-base alloys, the reader is referred to the special volume of "ASTM Standards on Copper and Copper Alloys," usually published annually by the American Society for Testing Materials.

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Chapter 26

Copper as an Alloying Element

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Apart from its major use in substantially pure form, and in brasses and bronzes, copper is an important alloying element in a large number of alloys that have a metal other than copper as the principal component. Phase diagrams for the alloy systems discussed in this chapter have been given in Chapter 22, and reference should be made thereto.

Copper in Aluminum Alloys

The aluminum alloy industry in the United States grew up around alloys containing copper as the major alloying constituent. Pure (99.9+ per cent) aluminum as cast has a tensile strength of only 9,000 psi, and a yield strength of 3,000 psi[1]. Strength in unwrought material is obtained by alloying, often followed by heat treatment.

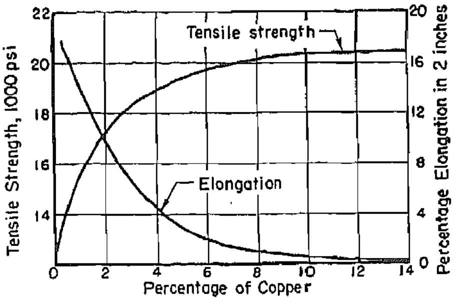

FIGURE 26-1. Tensile properties of aluminum-copper alloys as cast, determined on standard test bars cast in green sand[5]. (*Courtesy of the American Society for Metals.*)

Until sometime after 1911, it was believed that solid solutions were the strongest alloys possible. Additions of copper up to and somewhat beyond the limit of solid solubility (see Figure 26-1) strengthen aluminum rapidly. The 8 per cent copper alloy (No. 12) became the first standard general-purpose casting alloy, and a 10 per cent copper alloy (No. 122) came into use for pistons and other castings for elevated-temperature applications.

In 1911, the German metallurgist, Wilm, announced the development of duralumin. "Duralumin" was a name applied to various alloys containing about 4 per cent copper, 0.5 per cent magnesium, and 0.5 per cent manganese. The alloy was initially soft when quenched from about 500°C (930°F), but hardened spontaneously in a few days after quenching. Duralumin marked the real beginning of the strong wrought aluminum alloys. The composition was duplicated in other countries; the American version has been known as 17S.

Meanwhile, Merica[2] and his co-workers at the U. S. Bureau of Standards developed a rational theory to explain the hardening of duralumin. This theory postulated that the remarkable hardening was principally caused by incipient precipitation of very fine particles of $CuAl_2$. The phenomenon is known as "age hardening" or "precipitation hardening." Thus, the precipitation of this compound to form a two-phase structure was found to produce a stronger alloy than the solid solution, while retaining high ductility. The theory has since been generalized and broadened to explain similar hardening in many other types of alloys, and the accepted explanation of the mechanism whereby the precipitation results in hardening and strengthening has been considerably altered. To be possible, age hardening in an alloy requires that the solid solubility of a dissolved component be greater at an elevated temperature than at room temperature. If such an alloy is nearly saturated at the elevated temperature, quenched, and then reheated to an appropriate temperature, precipitation of the dissolved component will occur in a modified form. With duralumin and some other alloys, precipitation takes place at ordinary temperatures. However, spontaneous hardening is inhibited at temperatures sufficiently low.

Dix and Richardson[3] determined accurately the solidus line and solid solubility of copper in aluminum. Stockdale[4] showed that the precipitant of importance in duralumin-type alloys is not actually $CuAl_2$, but some six structures represented as (Al-Cu). The equilibrium diagrams of a large number of aluminum alloys, including those with copper, have been reviewed extensively by Fink[5].

Aluminum will dissolve 5.65 per cent of copper at 548°C (1018°F), the eutectic temperature, but will hold only 0.45 per cent in solution at equilibrium at 300°C (572°F) (see Figure 22-3, page 461). Other components, such as Mg_2Si, may reduce the solubility slightly[6].

The hardness of age-hardened alloys increases as the particle size of the precipitate decreases. Edwards, Frary, and Jeffries[1] reported the following relationship between hardness and particle size in a high-purity 4.5 per cent copper alloy:

	Brinell Hardness
Annealed, average diameter of particles of $CuAl_2$ about 0.00001 to 0.0001 inch	30
Quenched from 540°C (solid solution)	60
Quenched from 540°C and aged at 150°C, average diameter of particles of $CuAl_2$ about 0.0000001 inch	110

It was only natural that an improved casting alloy should result from a better understanding and appreciation of age hardening. About 1919 or 1920, a new casting alloy known as No. 195 was introduced. This was a 4 (later, 4.5) per cent copper alloy, with definitely controlled iron and silicon. A solution heat treatment followed by artificial aging is required to obtain maximum strength and hardness. Figure 26-2 shows the tensile strength of 4 per cent copper alloys after various heat treatments.

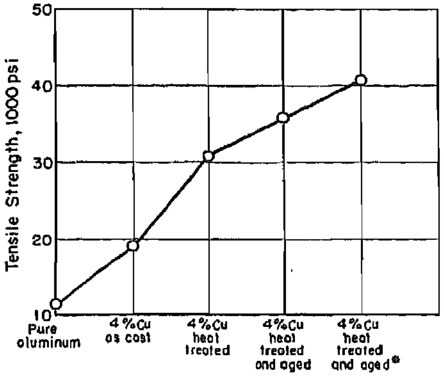

FIGURE 26-2. Effect on tensile strength of adding 4 per cent copper to aluminum and applying various heat treatments to the alloy[5]. (*Courtesy of the American Society for Metals.*)
* Aged to obtain maximum hardness.

The demand for still stronger light alloys continued and became imperative in the Second World War. Improved fabricating facilities had made it possible to roll and extrude alloys with higher magnesium content. The superduralumins, such as 24S, were ready to meet this demand. Alloy 24S is nominally 4.5 per cent copper, 0.6 per cent manganese, and 1.5 per cent magnesium. The alloy ages at room temperature similarly to and more rapidly than 17S, but unlike 17S, augmented strengths can be obtained from 24S with a solution heat treatment followed by cold work and artificial aging (*i.e.*, at an elevated temperature).

As early as 1926, especially in Germany, extra-strong aluminum-zinc-magnesium alloys had been developed, but their stress-corrosion rate was so high that the alloys were impractical. Near the end of the Second World War, however, Alcoa's 75S alloy was introduced[7, 8]. This new alloy contains 5.6 per cent zinc, 2.5 per cent magnesium, 1.6 per cent copper, 0.3 per cent (maximum) manganese, 0.25 per cent chromium, 0.2 per cent titanium. Somewhat similar alloys were introduced by other companies at about the same time. Although the newest strong wrought alloys contain copper, it is no longer the principal hardening element. These new alloys are widely used in aircraft construction, but the aluminum-copper-base alloys still continue to dominate the light alloy field. The addition of copper to aluminum, and still more the addition of zinc, decrease the resistance of the metal to atmospheric corrosion. Corrosion resistance is regained by covering or "cladding" the alloys with pure aluminum or corrosion-resistant alloys anodic to the stronger alloy. Cladding reduces the strength of the composite somewhat.

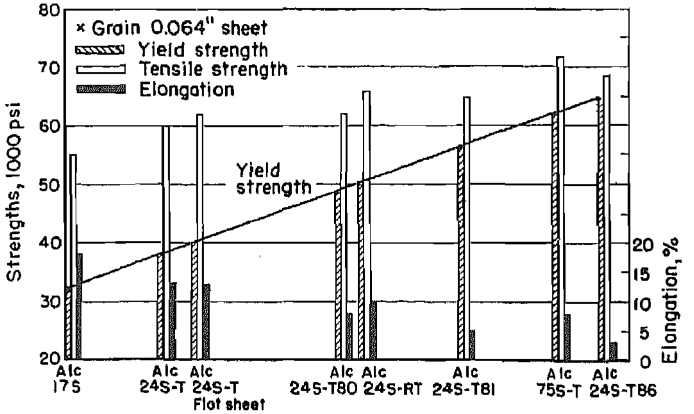

FIGURE 26-3. High-strength aluminum alloy Alclad sheet [7, 9]. (*Modified and reproduced by courtesy of the American Society for Metals.*)

Figure 26-3 shows mechanical properties of the clad high-strength aluminum alloys arranged in order of increasing yield strength[9]. Excepting only 75S, each of these alloys depends for its strength principally on the precipitation of a copper-aluminum compound from an alpha solid solution.

Copper in Ferrous Alloys

The constitution diagram of iron-copper alloys (*q.v.*) shows a peritectic at 96 per cent copper at 1094°C, 10°C above the melting point of copper, after which the melting point rises steeply until the composition reaches about 25 per cent iron. With more than 25 per cent iron the melting point rises gradually from about 1425°C (2600°F) to the melting point of iron at 1539°C (2800°F). No compounds are formed. Copper can dissolve 4 per cent iron in the epsilon phase at 1094°C (2000°F). The transformation from gamma iron to alpha iron takes place at 850°C (1560°F), at which temperature alpha iron can dissolve 1.4 per cent copper[10].

Pure copper and pure iron are miscible in the liquid phase in all proportions. The introduction of carbon affects the miscibility, however, so that a molten eutectic iron containing 4.3 per cent carbon can only dissolve about 3 per cent copper. The solubility of carbon in iron is practically unaffected by copper, but the Ar_1 and Ar_3 points are lowered about 10 to 15°C for each per cent of copper[11].

Ductile alloys can be produced throughout the entire composition range, but copper in commercially important iron-base alloys is limited to about 2.5 per cent, and is usually lower.

About 0.25 per cent of copper in copper-bearing steel will roughly double the corrosion resistance of the steel in air. Examination of the iron-copper diagram shows that while alpha iron will dissolve 1.4 per cent copper at the critical temperature, the solid solubility decreases to 0.25 per cent at normal temperatures. As a result, the condition necessary to make age hardening possible as described in the section on aluminum-copper alloys is met. Gregg and Daniloff[12] showed that a 0.08 per cent carbon, 1.01 per cent copper alloy rolled and then aged at approximately 540°C (1000°F) will show an increase in tensile and yield strengths of about 20,000 psi.

Precipitation hardening in copper-bearing steels, as in other alloys amenable to precipitation hardening, is controlled by both time and temperature. Smith and Palmer[13] investigated the precipitation hardening of two steels, each with about 1 per cent copper, but with 0.06 and 0.19 per cent carbon, respectively. Both attained maximum hardness after aging 15 minutes at 600°C (1110°F), or 2 hours at 550°C (1020°F), or 4 hours at 500°C (930°F). At 450°C (840°F) the low-carbon steel required 18 hours and the medium-carbon steel 32 hours to attain maximum hardness. In general, reheating copper-bearing steels to 480 to 540°C (896 to 1004°F) for about 4 hours is recommended for precipitation hardening[14]. Appreciable hardening begins with about 0.7 per cent and maximum hardening is obtained with about 1.5 per cent copper[13].

The mechanical properties of fully annealed copper-bearing steels were reported by Greenidge and Lorig[15].

Lorig[16] has summarized fully the effects of copper in steels. The summary includes data on hardness, tensile properties, and corrosion resistance. It is noted that the effect of copper on hardenability is similar to that of nickel. Copper increases the depth of hardening after quenching any steel, but its relative effect is much greater in the high-carbon than the low-carbon steels.

In cast iron, copper reduces the tendency toward chilling in light sections and at the same time promotes soundness in heavy sections. Copper may be substituted for silicon in cast iron, although normally more copper is required than the silicon displaced. Lorig and Adams[14] reported that addition of 2 per cent copper increased the strength of a low-carbon cupola iron 4,500 psi, a medium-carbon iron 6,000 psi, and a high-carbon iron about 7,000 psi.

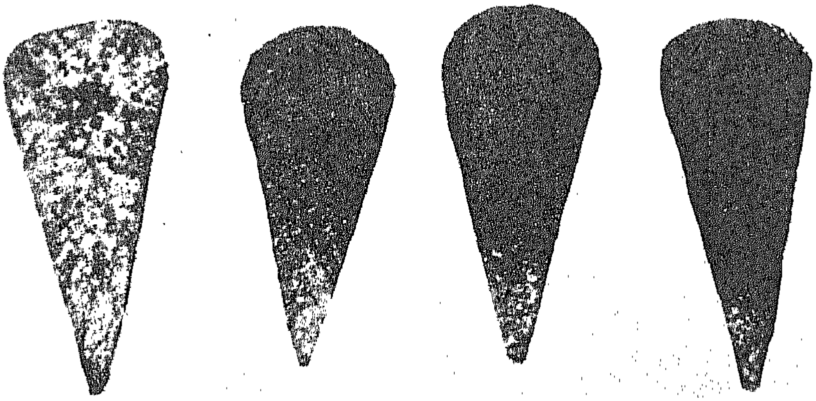

FIGURE 26-4. Chill bars showing progressive reduction of chill with increasing additions of copper (British Cast Iron Research Association). Approximately half size. (*Courtesy of the Copper Development Association.*)

Specimen Number:	*A412*	*A413*	*A414*	*A415*
Copper, per cent	0.00	0.82	1.78	2.43
Total carbon, per cent	3.23	3.13	3.13	3.09
Silicon, per cent	1.25			1.17
Manganese, per cent	0.54			0.46
Phosphorus, per cent	0.33			0.32

The marked effect of copper on graphitization in gray iron is illustrated by Figures 26-4 and 26-5, which are largely self-explanatory. Figure 26-4 shows four chill bars poured from the same base with increasing copper content. Figure 26-5 shows the effect of copper on hardness in a step-bar casting. The two figures together indicate that a balanced substitution of copper for silicon would permit making a chilled casting which could maintain full hardness and depth of chill in the chilled surface and simultaneously harden and toughen the matrix by the hardening effect of copper on pearlite and ferrite.

In castings containing copper above the solubility limit, the epsilon phase (practically pure copper) appears in the form of spherical particles, often visible to the naked eye. This primary copper has been found to refine effectively the graphite stringers by preventing the precipitation of coarse primary graphite in castings containing 6 to 8 per cent copper. As a result, very evenly distributed graphite precipitates later from the supercooled iron[17]. Although the British Cast Iron Research Association reports excellent refinement of graphite in cast iron by the addition of 6 to 8 per cent copper, the effect would probably be difficult to obtain in large ingots because of the tendency of iron-copper-carbon alloys to separate into two liquid layers in this region.

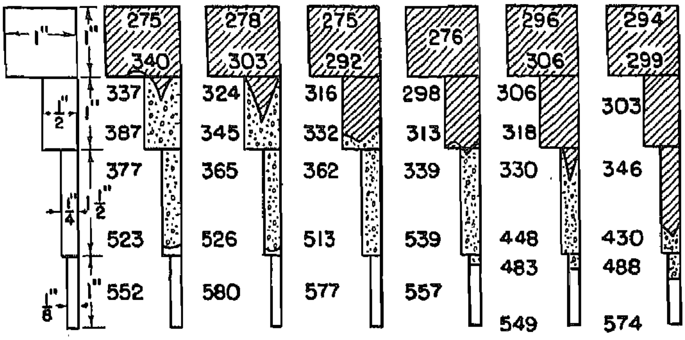

FIGURE 26-5. Step-bar castings with increasing percentages of copper (Sir W. G. Armstrong-Whitworth and Company, Ltd.) (*Courtesy of the Copper Development Association.*)

Copper, per cent:	0.07	0.56	0.61	0.80	1.21	1.52
Combined carbon, per cent (1-inch section)	1.08	1.08	1.00	0.90	0.88	0.99

Hardness figures: 1-inch and ½-inch section, Brinell hardness; ¼ and ⅛-inch section, Vickers diamond-point hardness.
Gray iron
Mottled iron
White iron

Analysis: Total carbon, 2.87 per cent; silicon, 1.54 per cent; manganese, 0.46 per cent.

With 15 per cent copper, the microstructure of low-carbon cast alloys shows copper filling interstices between the iron dendrites, as well as islands of primary copper. With increasing amounts of copper, the islands tend to disappear and the iron dendrites to separate until at about 30 per cent copper the matrix of the solidified alloy is found to be copper in which the iron occurs as fully formed dendrites that were grown in the still-liquid copper phase. Smith and Palmer[18] studied the entire range of copper-iron and found potentially useful alloys in the 50 to 60 per cent copper range. The wrought alloys were characterized by tensile strengths of 150,000 to 170,000 psi and 35 to 41 per cent IACS electrical conductivity. Were it not for the poor resistance of these alloys to atmospheric corrosion, they would be expected to find many applications in the communications field.

Gold-Copper Alloys[19, 20, 21]

The constitution diagram of gold-copper alloys shows a continuous series of solid solutions with a eutectic at 81.5 per cent gold, melting at 884°C (1623°F) (see Figure 22-5, p. 463). An ordered state (α′) with the ideal formula $AuCu_3$ (50.9 per cent Au) is formed from the alpha solid solution at temperatures below about 400°C (750°F) between the composition limits of 39.6 and 64.1 per cent gold. A similar ordered state (α″) with a tetragonal structure in place of the body-centered

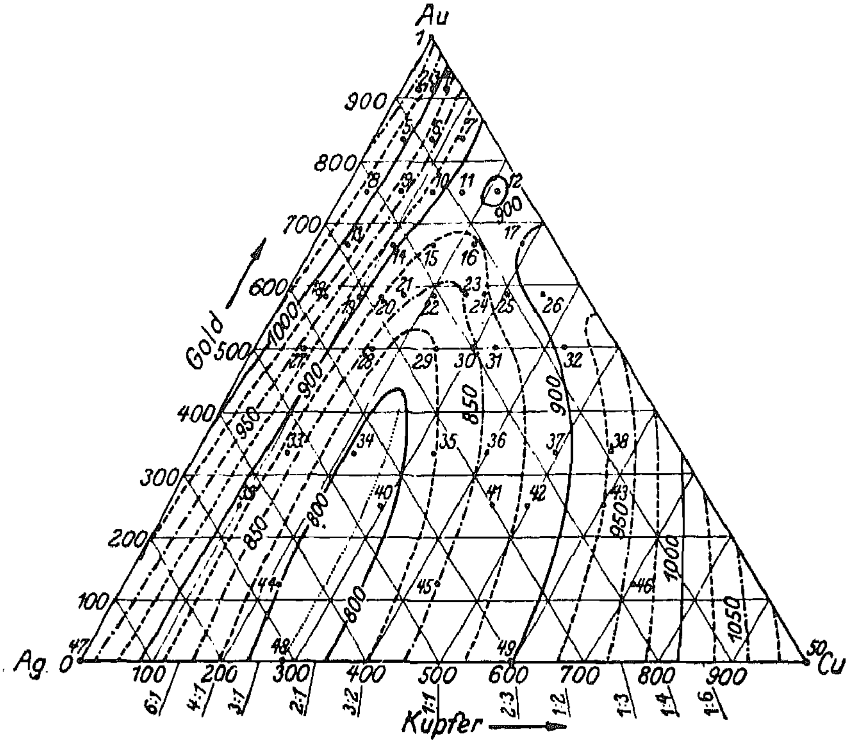

FIGURE 26-6. Melting points of gold-silver-copper alloys[23].

cubic structure of α and α′, and the ideal formula AuCu (75.5 per cent Au), is formed between 64.1 and 88.4 per cent Au. The commercially important 18-carat gold alloys may suffer hardening and loss of ductility from the AuCu ordering phenomena. Raub[22] discusses the binary gold-copper alloys in detail. A number of photomicrographs of various crystal structures are shown, and an extensive bibliography is included.

Copper hardens gold principally by forming solid solutions, but the phenomenon of low-temperature atomic rearrangement termed "ordering" permits substantial age hardening. This phenomenon and the resulting age hardening is carried over to the gold-copper-silver alloys—the green, yellow, and red golds of the jewelry trade. Aging is induced by heating the quenched alloys for ½ to 2 hours at 200 to 350°C (390 to 660°F) or by slow cooling, depending on the alloys.

The gold-copper-silver alloys are more commonly used than the gold-copper alloys. An 18-carat alloy of 75 per cent gold with about equal parts of silver and copper has a yellow color; replacing more of the silver with copper produces a red gold. The 14-carat 58.35 per cent gold, 2.5 to

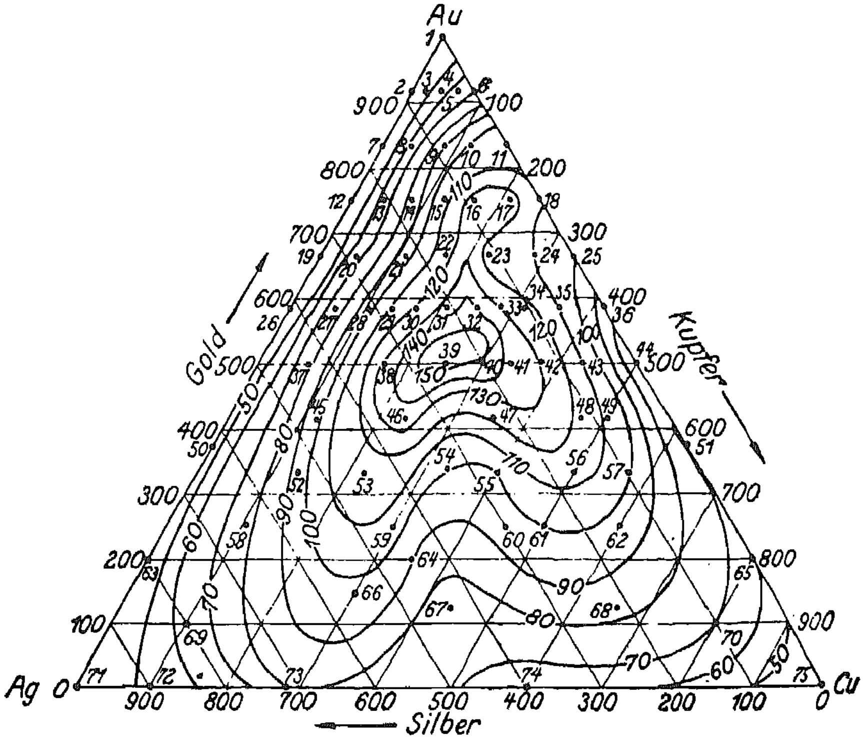

FIGURE 26-7. Brinell hardnesses of gold-silver-copper alloys[23].

5 per cent copper, balance silver, alloy is green. Increasing the copper to 20 to 30 per cent makes yellow golds and higher copper produces a reddish color. The 10-carat golds are largely high-copper alloys with various additions to control the color. The effect of copper on the melting point and hardness of these ternary alloys is shown in Figures 26-6 and 26-7, taken from Sterner-Rainer[23]. "White gold" is a series of gold-nickel-copper-zinc alloys; "pink gold" is a series of gold-silver-copper-nickel-zinc alloys containing the requisite amount of gold to make 10-, 12-, and 14-carat alloys. The copper varies from 51.5 to 31.0 per cent.

Nickel-Copper Alloys[24, 25]

Copper is soluble in nickel in both the liquid and solid states in all proportions. No compounds are formed and no eutectic occurs. Therefore, all of the alloys exhibit homogeneous structures, regardless of the heat treatment. Although all of the alloys are ductile, only monel and constantan have much commercial utilization. In addition to these two more important alloys, a third alloy, 70 Ni-30 Cu, is used in the form of wire or ribbon for magnetic temperature compensation in electrical meters that depend on the flux produced by a constant voltage or by a certain load current for their actuation.

Monel is the most important nickel-copper alloy. It is available in both cast and wrought form. This alloy, with 67 per cent nickel, 30 per cent copper, balance iron and manganese, is a strong, ductile alloy that can be formed into rod, wire, plate, sheet, strip, and tubing. Ingots are cast of this alloy that weigh up to 14,000 pounds. The tensile strength varies from 70,000 psi in the annealed state to 120,000 to 140,000 psi in the full-hard condition. The mechanical properties are quite stable with temperatures up to 400°C (750°F). Monel is widely used in chemical, pharmaceutical, and marine equipment, laundries, and kitchens because of its pleasing appearance, strength, and resistance to sea water, dilute sulfuric acid, and strong caustics.

Several variations of the basic monel composition have been developed for special applications. Among these are "K" monel, containing added aluminum and silicon, which make the alloy age hardenable. "H" monel and "S" monel with silicon and iron are casting alloys. Specific compositions and mechanical properties are shown in Tables 26-1 to 26-3[26].

The other important nickel-copper alloy is constantan. Constantan is an alloy of 45 per cent nickel with 55 per cent copper* that is distinguished by its high electrical resistance and unusually constant temperature coefficient of electrical resistivity. This coefficient is ±0.00002 over

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* Although more than 50 per cent copper, constantan is listed by the National Bureau of Standards and by the American Society for Metals as a nickel-base alloy.

TABLE 26-1. NOMINAL CHEMICAL COMPOSITION OF MONEL[26]

Material	Nickel,* %	Copper, %	Iron, %	Manganese, %	Silicon, %	Carbon, %	Sulfur, %	Aluminum, %
Monel	67.0	30.0	1.4	1.0	0.1	0.15	—	—
R-monel	67.0	30.0	1.7	1.1	0.05	0.10	0.035	—
K-monel	66.0	29.0	0.9	0.85	1.0	0.15	—	2.75
KR-monel	66.0	29.0	0.9	0.85	1.0	0.30	—	2.75
H-monel	65.0	29.5	1.5	0.9	3.0	0.30	—	—
S-monel	63.0	30.0	2.0	0.9	4.0	0.10	—	—

* Includes approximately 0.75 per cent of nickel content as cobalt.

TABLE 26-2. MECHANICAL PROPERTIES OF WROUGHT MONEL[26]

Material	Yield Strength, 0.2% Offset, psi 10^3	Tensile Strength, psi 10^3	Elongation in 2 Inches, per cent	Reduction of Area, per cent	Hardness, Brinell	Charpy Impact, Ft-Lb
Monel	25-160	70-170	50-2	75-50	110-250	220-150
R-monel	25-130	70-140	50-4	70-50	110-230	196-140
K-monel	40-175	90-200	45-2	70-25	140-320	170-42[a]
KR-monel	40-175	90-200	45-2	70-25	140-320	—

[a] Specimens fractured completely.

TABLE 26-3. MECHANICAL PROPERTIES OF CAST MONEL[26]

Material	Yield Strength, 0.2% Offset, psi 10^3	Tensile Strength, psi 10^3	Elongation in 2 Inches, per cent	Hardness, Brinell	Izod Impact, Ft-Lb
Monel	32.5-40	65-90	45-25	125-150	80-65
H-monel	45-75	90-115	20-10	175-250	45-35
S-monel	80-115	110-145	4-1	275-375	9-1

the range of 20 to 100°C and only ±0.000025 over the range of 0 to 500°C, in the wrought form. Extensive use is made of this property in electrical instruments. Constantan is not ordinarily used for resistance-heating elements, since it deteriorates rapidly in air at temperatures above 500°C (930°F), although it can withstand short exposures to higher temperatures.

An excellent summary of the properties of the nickel-copper alloys has been published by the National Bureau of Standards[27].

Silver-Copper Alloys

The silver-copper system is relatively simple, with a eutectic at 28.1 per cent copper which solidifies at 779.4°C (1435°F) (see Figure 22-1,

p. 459). The maximum solid solubility of copper in silver at this temperature is 8.8 per cent, decreasing to about 0.1 per cent in equilibrium at room temperature.

The high-silver silver-copper alloys can be age hardened. They have been considered to be the classical example of age hardening by precipitation of finely divided particles with simultaneous changes in physical properties. The aluminum-copper alloys were considered to harden without actual precipitation (the knot theory)[28]. However, Cohen[29] and later Gayler and Carrington[30], showed that the two processes are not independent, but that knot hardening precedes precipitation hardening. In practice, the artificial aging can be stopped with any particular alloy wherever the maximum hardening effect is obtained.

All of the alloys of silver and copper are ductile. Of the high-silver alloys, the most important is the 92.5 silver-7.5 copper alloy known as sterling silver. The alloy is universally prized for making flat ware and objects of art. It can be age hardened, resulting in a considerable gain in yield strength.

An alloy containing 8.72 per cent copper, balance silver, annealed at 750°C (1380°F) for 160 hours and quenched, had a Rockwell F hardness of 68. Maximum hardness of RF105 was obtained after aging at 150°C (300°F) for 500 hours, or at 125°C (257°F) for more than 1,000 hours. Aging the alloy at 200°C (390°F), the maximum hardness was RF95, reached after 18 hours[29].

The other important silver alloy is 90 silver-10 copper, or coin silver. This alloy, having more copper than can be retained in solution, has a duplex structure regardless of the heat treatment. The alloy is used for silver coinage in the United States and for electrical contacts where a harder material than pure silver is desired.

The eutectic silver-copper alloy (28 per cent Cu) is used to some extent as a brazing metal.

Wise[31] has collected much of the available information on silver-copper alloys. His diagrams show that strength of the annealed and quenched alloys increases with copper content up to about 43,000 psi at about 7 per cent copper and remains constant with added copper up to 20 per cent. Maximum strength of approximately 54,000 psi is shown for a 7.5 per cent copper alloy quenched and aged 2½ hours at 280°C (536°F). The corresponding Brinell hardness is about 103. The maximum obtainable Brinell hardness is indicated as above 150 in the 7.5 per cent copper alloy. These data are taken from Frankel and Schaller[32].

Palladium-Copper and Platinum-Copper Alloys[33]

Both palladium and platinum form a continuous series of solid solutions with copper (see Figures 22-24 and 22-25, p. 478 and 479). Although the alloys are potentially useful, little actual demand exists for the binary alloys. At about 600°C (1110°F) in the range of 41 to 51 per cent Cu, face-centered cubic alpha palladium-copper transforms to the body-centered cubic beta phase with an ordered structure. Some beta phase coexists with the alpha phase over a range of 10 weight per cent on each side of the range shown. Other ordering transformations occur in the range of about 62 to 87 per cent Cu, but no new phases are known to form. The 60 palladium-40 per cent copper alloy has some use as electrical contacts. The ternary palladium-silver-copper alloys with more than 5 per cent Cu and not more than 65 per cent Pd are age hardenable. The highest hardness is reached with about 30 Cu, 30 Ag, 60 Pd. Use is made of the ternary alloys in dentistry. Platinum-copper alloys show ordering transformations over most of the composition range.

Zinc-Copper Alloys

The copper-zinc alloys today are among the most important in the nonferrous field, but the high-zinc Zn-Cu alloys are of lesser importance commercially. The high-zinc end of the copper-zinc constitution diagram is extremely complex (see Figure 22-36, p. 487). Beta-gamma brass and gamma brass show a cubic crystal structure. Delta brass with less than 78.5 per cent of zinc breaks down to gamma-epsilon brass. At the moment of inversion to epsilon brass, a notable volume expansion takes place. Epsilon and eta brasses, like pure zinc, have a close-packed hexagonal structure. Iokibe[34] investigated this expansion, first reported by Turner and Murray*, and found that all of the alloys with between 70 and 95 per cent zinc expand. A series of sand-cast specimens showed a sharp maximum in expansion as the composition reached about 85 per cent zinc. Microscopic voids are left in the metal between the epsilon dendrites. If expansion is prevented by use of an iron mold, inverse segregation takes place, concentrating copper toward the center of the ingot. This tendency toward expansion is probably important in commercial die-casting alloys, causing them to fill the molds completely.

The alloys of zinc and copper containing up to 10 per cent copper can be hot rolled to 70 per cent reduction of area without excessive edge cracking[35]. Breaking stress of the hot-rolled alloy is nearly doubled and elongation is increased from 25 to 40 per cent by the first 1 per cent of copper; little change is noted with the next 1 per cent, and thereafter the strength increases and elongation decreases with further additions to 67,000 psi with zero elongation at 9 per cent copper[36]. Messner[37] studied the creep resistance of 1 per cent and 4 per cent copper die-cast zinc alloys at 20°C. He estimated that the drawn 4 per cent alloy would reach 1 per cent elongation after 10,000 hours under a load of 3,750 psi. As cast, the same extension was expected to be reached by the 1 per cent alloy with a load of 750 psi and the 4 per cent alloy with 700 psi. The values were increased to 1,700 and 1,600 psi, respectively, by annealing.

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* *J. Inst. Metals*, 2, 98 (1909).

An extruded German alloy, Giesche Z. L. 7, containing 4 per cent copper, 0.2 per cent aluminum, is said to have had its strength increased 15 to 20 per cent and its elongation increased 100 per cent by pressing or forging in the direction of the original extrusion. Worked in this manner, the alloys could withstand all of the processes normally applied to 70-30 and 60-40 brass, although the speed of working had to be reduced. Allowing for notch brittleness in design, the alloy could replace 60-40 brass if necessary[38]. The mechanical properties of some binary zinc-copper alloys are shown in Table 26-4.

TABLE 26-4. MECHANICAL PROPERTIES OF ZINC-COPPER ALLOYS[38]

Composition, per cent Cu	0.1% Proof Stress, psi	Tensile Strength, psi	Elongation, per cent	Reduction of Area, per cent	Impact Resistance, Ft-Lb	Brinell Hardness
1	16,600	30,500	37	76	3.3	58
2	17,000	37,400	33	76	3.5	67
3	16,600	41,300	50	80	3.5	71
4	14,300	42,600	41	73	3.0	80
5	12,300	44,100	43	67	1.1	89

Addition of up to 0.05 per cent of magnesium increases the resistance of the zinc-copper alloys to corrosion.

A zinc-1 per cent copper alloy (Zilloy-40) is produced commercially in the United States. "The Metals Handbook" shows a tensile strength for hot-rolled strip of 24,000 psi parallel to the rolling direction and 32,000 psi perpendicular to the rolling direction. Cold-rolled strip is 8,000 psi stronger in each direction. Addition of 0.01 per cent magnesium increases the strength by 4,000 to 8,000 psi. Both alloys have excellent resistance to atmospheric corrosion.

Much more important than the binary zinc-copper alloys are the ternary zinc-copper-aluminum alloys. In the high-zinc corner of the Al-Cu-Zn diagram, "the (Cu-Al) phase is not found in equilibrium with (Zn), and the ε (Cu-Zn) phase is found to coexist with the (Zn) and the (Al) phases"[39]. In this system, the most important alloys commercially are known as "Zamak 2" and "Zamak 5." These die-casting alloys are widely used in the automotive, electrical, and other industries. Identical alloys are used in European countries. Some properties of these alloys are shown in Table 26-5.

TABLE 26-5. PROPERTIES OF ZINC DIE-CASTING ALLOYS[40]

Trade Name	"Zamak 2"	"Zamak 5"
ASTM number	XXI	XXV
Composition (bal. Zn), %	Al 4.1, Cu 2.7, Mg 0.03	Al 4.1, Cu 1, Mg 0.04
Density	6.7	6.7
Melting point, °C	379.3	380.4
Tensile strength, 1000 psi	52.1	47.6
Elongation, %	8.0	7.0
Brinell hardness	100.0	91.0

"Zamak 2" has good hardness and tensile strength. "Zamak 5" resists shock better and has better dimensional stability. Both are reasonably corrosion resistant. The tensile strength of "Zamak 2" increases after aging at 95°C (200°F), while that of "Zamak 5" decreases slightly. The shock resistance of "Zamak 2" drops to one-third of its original value after aging, while that of "Zamak 5" drops less. For both, however, the values remain above those of ordinary gray iron. Below 0°C the shock resistance of both alloys drops rapidly. "Zamak 2" is becoming obsolete for die casting, but is still widely used for sand casting. Over a period of years "Zamak 5" shrinks a maximum of 0.0009 inch per inch. Low-temperature annealing treatments will cause about two-thirds of this shrinkage to take place at once.

Copper in Other Alloys

At the high-tin corner of the tin-antimony-copper diagram, Cu_6Sn_5 begins to precipitate from a ternary solid solution at about 0.75 per cent copper so long as the antimony remains below about 7.5 per cent. With greater amounts of antimony, primary Cu_6Sn_5 and secondary SbSn are precipitated[41]. All of the common high-tin babbitt metals lie in one or the other of these fields. The fatigue strength and the indentation hardness of the alloys both increase with increasing antimony and copper. However, the maximum resistance to cracking in service is obtained with about 3 to 7 per cent antimony and 2 to 4 per cent copper. Large rigid bearings may have higher alloy contents[42]. Mantell[43] reported that a 93.0 Sn-3.5 Sb-3.5 Cu alloy has tensile and yield strengths, respectively, of 8.1 and 5.6 kg per square millimeter, 11.6 per cent elongation, and Brinell hardness at 20°C of 24.9, dropping slowly to 22.8 at 90°C.

The bond strength of babbitt metals cast on steel is high for babbitts with about 3½ per cent copper, but drops more than 40 per cent when the copper is increased to 7 per cent. Forrester and Greenfield[44] showed that the decreased bond strength is associated with precipitation of

Cu_6Sn_5 at the interface of the babbitt and the steel, where the compound concentrates during freezing by normal segregation.

Tin-lead-antimony-copper alloys are also used for bearings, but are considered inferior to the high-tin alloys[42]. The compositions of three of these alloys are:

ASTM No. 4: 75 Sn, 10 Pb, 12 Sb, 3 Cu
ASTM No. 5: 65 Sn, 18 Pb, 15 Sb, 2 Cu
ASTM No. 6: 20 Sn, 63.5 Pb, 15 Sb, 1.5 Cu

Mantell's list of lead-base bearing alloys shows copper varying from 0.2 to 7.4 per cent. Pewter may also contain a little copper as a hardener. Type metals may contain 0 to 4.7 per cent of copper. The zinc-tin bearing metals, Britannia metal, and various white casting alloys usually contain from 2 to 11 per cent copper[43].

Copper is added to manganese alloys in amounts from 3.5 to 35 per cent to increase the elongation.

The silver-copper-zinc alloys in which the copper varies from 0 to 40 per cent are widely used as "silver solders."

The mechanical properties of a great number of ferrous and nonferrous alloys, many of which contain copper as a minor constituent, have been published by the National Bureau of Standards[45].

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Chapter 27

The Melting and Casting of Copper-Base Alloys

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MELTING

Since the nonferrous foundries in operation today vary greatly in size and in the nature of their operations, no one type of melting furnace can be recommended in preference to another. The function of the melting furnace is to supply molten metal to the mold when needed, of the best possible quality, at the proper temperature, and at the lowest possible cost. These factors, together with desirable working conditions, determine the choice of melting equipment and the manner in which it is to be operated.

The prime object in nonferrous melting is to charge good metal into the furnace and deliver it to the mold as molten metal without impairment; therefore, little or no consideration should be given by the brass and bronze foundryman to refining the metal while it is being melted. It has become nearly universal in recent years to use prealloyed composition ingot. Alloy ingot to meet any desired specification is readily obtainable and the melter, therefore, has no need to bother with alloying or refining procedures. However, frequent chemical analyses and physical tests should be made to make certain that the ingot is of satisfactory quality.

The final choice as to size and type of furnace to be used depends primarily upon the following:

(1) The volume of production.
(2) The size and number of castings.

(3) The nature and characteristics of the alloys in use, and whether there are frequent changes from one alloy to another.

(4) Availability and cost of different fuels.

Regardless of the type of melting equipment chosen, the size should be dependent upon the weight of the castings to be poured and upon the number of molds to be poured from a single furnace heat. If the metal is melted in a crucible which is also used to pour the molds, *i.e.*, a lift-out crucible furnace, the capacity of the crucible should be such that the first and last metal poured remain within a prescribed temperature range, as the temperature drop may be considerable and have pronounced effects on the castings. If the molds are poured from a ladle which receives its molten metal from a hearth-type or tilting crucible furnace, the capacity of the furnace should equal the capacity of the ladle multiplied by the number of pouring crews used to empty the furnace. In this way the furnace may be emptied and back in production without delay.

Fuel-fired Furnaces

This class of furnaces is differentiated from the electric furnaces in that combustible hydrocarbons such as oil, gas, coke, or coal are used as fuel. They are of the following general types:

(1) Crucible-pit
(2) Crucible-tilting
(3) Open flame
(4) Reverberatory
(5) Cupola

Fuel-fired furnaces are less expensive to install than electric furnaces and require less skilled maintenance and technical supervision, but do require more skill and experience on the part of the melter. As a rule, the working conditions are not as favorable as those around an electric furnace.

Crucible-pit Furnace. This type of furnace is well adapted for use where a variety of alloys in relatively small quantities are to be melted. The capacity of the crucible is usually 250 pounds or less and is not only used for the melting but also as the pouring ladle. Crucibles are expensive, though long-lived with proper handling and care. Judgment should be used in discarding worn crucibles before actual failure, since failure in service is likely to have serious consequences. Gas or oil is the usual fuel in present-day practice, although some foundries still use coke or coal. The furnace may be either set on the floor or in a pit with the top of the furnace at floor level.

Tilting Crucible Furnace. Furnaces of this type usually have a capacity sufficient to fill two or three 250-pound ladles, which makes them well adapted for production use. Almost without exception, gas or oil is the only fuel used. The combustion space between the crucible and furnace lining is a critical factor and must be maintained with care when linings are patched or replacements made. Suitable precautions are necessary to prevent crucible breakage during charging of heavy metal and to replace worn crucibles before actual failure, which may cause damage to the lining and lost production time.

Open-flame Furnace. These furnaces are of many sizes and shapes, mostly cylindrical, and may be either of the stationary or rotating type. They are rapid melters and except for rather high melting losses, the operating costs are relatively low. Since the flame and products of combustion are in direct contact with the metal, considerable skill on the part of the melter is required to maintain a high degree of metal quality.

Reverberatory Furnace. These furnaces may range in capacity from a few hundred pounds up to several tons and are characterized by a shallow refractory hearth. In some furnaces, provision is made for preheating or actually melting the metal before it reaches the hearth, which makes them very rapid melters. In general, the precautions for their use are similar to those mentioned for the open-flame furnaces.

Cupola Furnace. This type of furnace has not found much use in the copper-base alloy foundry, except in the melting of the high-lead tin bronzes for bearings. Since the metal is in direct contact with the fuel, a special grade of coke having low ash and sulfur must be used. Because of oxidation and volatilization of some of the alloying metals, additions must be made to the ladle to compensate for these losses, which are not always predictable.

Electric Furnaces

Most large brass foundries make some use of electric furnaces, and some foundries use no other type. The initial investment for an electric furnace installation is high; however, when they are properly operated with steady use, the cost of operation is relatively low. Skilled labor is required for the installation and maintenance of the refractory linings and electrical and mechanical equipment connected with the furnace. The electric furnaces also have the best working conditions of all the furnaces used in brass foundries, primarily due to the absence of any combustion gases in the melting area.

Of the electric-furnace types discussed below, only the first two are in general use, with the last two in less frequent use.

Indirect-arc Furnace. This type of furnace usually oscillates or rocks during melting to insure a thorough mixing of the charge and uniform distribution of the heat. The graphite electrodes used must be of high quality, must fit the electrode port openings closely, and must be kept dry. Impairment of metal quality may be caused by one or more of the following:

(1) Smoky arc, caused by variable and low voltage.

(2) Oil or water in the metal charge or moisture in the refractory lining, causing gas porosity.

(3) Silicon carbide or water glass in the refractory that might break down chemically in the incandescent arc, causing a pickup of impurities in the metal.

Under properly trained supervision, these furnaces are rapid melters and will give molten metal of consistently high quality.

Low-frequency Induction Furnace. The induction channel in this furnace must be thoroughly preheated and then filled with molten metal of the desired composition previously melted elsewhere, before further charging and melting. The furnace is never completely emptied from one heat to another, so that a flow of electric current may be maintained through the molten metal in the induction channel. The furnace is particularly well adapted to the melting of high-zinc alloys such as yellow brass and manganese bronze because of the low losses of zinc.

High-frequency Induction Furnace. This furnace is essentially a crucible furnace, and in one of its designs employs a removable crucible. It thus has the flexibility of the fuel-fired crucible furnace, but has the advantage of a much faster rate of melting. The furnace is well adapted for intermittent use on a wide variety of alloys.

Indirect Resistance Furnace. The construction of this furnace is almost identical with that of the indirect-arc furnace, except that an incandescent graphite bar takes the place of the electric arc as the source of heat. It was primarily designed for the melting of manganese bronze and other high-zinc alloys because of the small losses of zinc.

Due to the fact that the refractory linings in the indirect-arc, indirect resistor, and the low-frequency induction furnaces all absorb considerable amounts of heat, they are best suited for almost continuous operation because of the high operational efficiency attained.

Metal Quality

Metal of good quality may be obtained from any of the furnaces mentioned, if the proper operating procedure for each is understood and carefully followed. The impairment of metal quality during melting may come from the following sources:

(1) Contact with the refractory or crucible.

In the case of the indirect-arc furnace, mention has already been made of certain materials that should not be used as linings in that furnace.

Normally, such extreme caution is not necessary for most furnaces do not subject the lining or crucible to such intense or localized heating.

(2) Foreign materials introduced with the charge or during melting. In shifting from one charge to another, it sometimes happens that an important constituent in the first alloy may be an undesirable impurity in the second. This is not particularly important in crucible melting but requires the use of a "wash" heat in any of the hearth-type furnaces.

Good practice requires that the metal charged to the furnace should be free of foreign materials, particularly moisture, oil, or any organic material. Sand adhering to foundry returns is not likely to cause trouble, though some foundries take the precaution of cleaning the returns by blasting before melting.

(3) Furnace atmosphere.

In fuel-fired furnaces care is taken to maintain a slightly oxidizing atmosphere, preferably 0.1 to 0.5 per cent excess oxygen, to insure the absence of unburnt fuel. The presence of unburnt fuel is usually associated with what is termed "gassy metal," which gives a porous open structure in the cast metal, thereby lowering its quality. Highly oxidizing atmospheres should also be avoided because of excessive melting losses. In certain types of reverberatory furnaces where the melting time is very short, 20 minutes or less, reducing atmospheres are often used.

In electric furnaces it is both possible and desirable to operate with a neutral atmosphere. However, care should be taken to avoid the presence of moisture from such sources as wet metal turnings, damp charcoal, or moist, recently patched linings.

Another source of "gas" trouble comes from the use of ladles with rammed linings that have not been preheated sufficiently. It is common practice to bake the new ladles several hours before the preheating that immediately precedes its use.

Fluxes

If good metal is used and proper melting practices maintained, the regular use of fluxes in melting brass and bronze alloys is unnecessary. Certain alloys, such as monel and nickel silvers, are usually protected by a liquid glass cover during melting. The continuous use of so-called purifying fluxes can be recommended only as a safeguard against the results of careless melting practices.

Since it is a recommended procedure to use an oxidizing flame during melting, some of the metal becomes oxidized and the use of a deoxidizer is advisable. Phosphor-copper (15 per cent phosphorus) is generally used for this purpose for red brasses and tin bronzes, usually not to exceed 2 ounces per 100 pounds of metal. The phosphor-copper is added in the pouring ladle or crucible and thoroughly stirred. In normal practice, deoxidizers are not required for the aluminum, manganese, or silicon bronzes.

Temperature Control

It is desirable not to overheat the metal or hold it in the furnace any longer than necessary because of the danger of dissolving harmful gases. As a rule, this is subject to the melter's judgment and he must make sure that the metal is hot enough. In fuel-fired furnaces, the melter has little to guide his judgment and molten metal temperatures in excess of 110°C (200°F) above the desired pouring temperature are not uncommon. In electric furnaces the operator is greatly aided by the switchboard instruments and maximum temperatures no more than 30 to 45°C (50 to 75°F) above the desired temperature can be attained consistently.

Pyrometers are now widely used for measuring temperatures in the pouring crucibles or ladle and are essential to good foundry practice. The red brasses and tin bronzes are particularly sensitive to pouring temperatures. Once a pouring temperature for a particular casting is decided upon, it should be adhered to rigidly as long as no change is made in the casting or gating design.

CASTING

Sand Casting

Sand casting, with the lowest pattern cost and widest dimensional tolerances, is the cheapest and most widely used method of producing copper-alloy castings in varying quantities. The process is most flexible in its ability to produce various designs and sizes of castings, as well as to handle the variety of alloys that may be cast in this way. Sand casting offers the fewest limitations and castings can be obtained most rapidly by this process. In some respects, however, sand castings do not compare with castings made by other methods; the surface obtained is the least desirable, casting tolerances are much greater, and density is only intermediate.

Allowances. As with any casting method, the sections should be as uniform as possible, with proper fillets, draft, and machining allowances. The practical minimum section is about $\frac{3}{32}$ inch, but the casting should not be thin over too great a length in order to avoid "misruns" or "cold shuts." The draft angle on the pattern should be about 3 degrees. Finish allowances should be $\frac{1}{16}$ inch for sections up to 1 foot, $\frac{1}{8}$ inch from 1 to 2 feet, $\frac{3}{32}$ inch from 2 to 3 feet. Shrinkage of $\frac{3}{16}$ inch per foot is usual for most copper-base alloys.

Gating. The gating system should insure that the metal enters the mold as quietly as possible in order to minimize the formation of dross from metal agitation. The size of the sprue should be related to the runner and the gate, so that the sprue may be kept filled by pouring at a fairly uniform rate. Runners should be free from sharp corners and edges and the in-gates should be well filleted.

In both the design of the casting and the gating system, consideration should be given to directional solidification, in order that the portion of the casting furthest from the gate will freeze first and the heaviest section, at the gate, will freeze last. The risers must remain fluid the longest, in order to supply liquid metal to feed the heavy section of the casting. When the liquid metal comes to rest in the mold cavity, the metal in the riser should be hotter and remain hotter than that in the casting. This may be accomplished in several ways:

(1) Gating in such a manner as to have the riser receive the last metal poured.

(2) Using chills at heavy sections in the casting to promote more rapid cooling.

(3) Using insulating sleeves on risers to keep the metal in the riser liquid a longer length of time.

Certain alloys, such as the high-strength brasses and aluminum and silicon bronzes, have higher localized liquid shrinkage and require larger risers than the red brasses or tin bronzes.

Sands. For most of the copper-base alloys, refractoriness of the molding sand is not of great importance, as the average sand has adequate high-temperature properties. The bonding material in the sand must be one which will maintain its bonding qualities through repeated use. "Natural" molding sands (sand as mined having sufficient natural bond), are in predominant use in the brass foundry, though the use of "synthetic" molding sands (clay-free silica sand bonded artificially) has become popular because of the inconsistency in properties of the natural sands.

For best results, control of various sand properties is necessary. Daily tests of green strength, permeability, and moisture content should be made and corrective measures taken to keep these properties at the optimum conditions.

The usual recommendation for cores for brass and bronze alloys is to use a new sharp silica sand (very little clay) and a straight oil binder. The amount of core oil used should be kept at a minimum and a ratio greater than 1 of oil to 40 of sand is seldom necessary. Molding sand is sometimes added to increase the green strength of the core and additives such as dextrine, wood flour, kerosene, etc., impart certain desired properties to the green or baked core. Baking of the core consists of removing the water and volatile matter by evaporation and finally oxidizing the oil to create the oil-residue bond.

Facing sands and mold or core washes are not normally required, except for the high-lead bronzes and phosphor bronzes. These alloys "burn-in" or penetrate into most molding and core sands, hence some refractory coating material is required to keep this to a minimum.

Molding. Hand molding, as compared to machine molding, requires molders with the greatest skill in order to get results, especially when gates must be cut and loose patterns used. Split patterns may be mounted on boards to save time and reduce the skill required. At best, hand molding gives least uniformity.

Machine molding gives uniform molds with greater daily production and requires less skill on the part of the molder. It is possible to make temporary mounts of patterns and gating and to derive the benefits of machine molding without the expenditure of a large amount of money for pattern equipment. For best results and production, metal patterns should be mounted on metal plates or cast aluminum match plates should be used.

The molding machines are usually classified into either jolt, squeeze, jolt-squeeze, or slinger. This classification is based on the method used to ram the sand around the pattern and in the flask.

Pouring. Metal that is melted in the stationary crucible furnaces is usually poured from the crucible directly into the mold. For transporting metal from the larger furnaces, the best pouring vessel is an insulated ladle lined with either a ramming mixture or preformed refractory. Such ladles have high initial cost, but this is offset by long life and low loss of temperature while pouring. Crucibles and ladles should be dried thoroughly and preheated before use.

The lip of the pouring vessel should be held as close as possible to the sprue opening and the metal should be introduced with a minimum of agitation. The sprue can be shaped to minimize swirling. The first metal should be poured directly into the center of the sprue, not splashed around the rim, and the sprue should be kept filled during the pour.

Pouring Temperature. One of the most important factors in the production of sound copper-base alloy castings, especially those for pressure work, is that of pouring temperature. The optimum temperature is the lowest one that will produce sound castings, that is, that temperature at which the casting will "run" and no internal shrinkage will occur. Temperature control has been mentioned in a previous paragraph.

Cleaning. Most of the sand adhering to the castings on shakeout may be removed by rapping them lightly. Care should be taken not to break up the cores at this point, in order to prevent contamination of the molding sand with core sand. After removal of the cores, the castings may be cleaned of the tightly adhering sand by tumbling, water blasting, sand blasting, or merely by scratch brushing.

Gates and risers on the casting may be removed by sprue cutters, hand or band saws, or friction wheels. The type of equipment chosen depends upon the size and thickness of the section to be cut. The sprue cutter is fast, economical, and is preferred for those jobs that have many small castings attached to a single runner. Friction wheels are necessary for the removal of large, bulky risers and for the removal of gates and risers of the harder alloys.

Defects. There are many types of defects which occur in copper-base alloy castings, some of which are due to a single cause, whereas others result from a combination of causes. A committee of the American Foundrymen's Society reported on Analysis of Defects in 1938*. A good brass foundryman must have the ability to classify defects and then apply the required remedial measures.

Permanent-mold Casting

Permanent-mold casting may be defined as the art of producing castings on a repetitive basis in metal molds operated by hand or mechanically, with or without sand cores and without the application of any external pressure. Although the life of a permanent mold is long and a unit may be used repeatedly, the mold can hardly be considered permanent. Mold cost is high and many factors should be considered before choosing the process for a particular casting. In general, 500 castings should be regarded as a minimum number for which a permanent mold may be built economically.

Permanent-mold castings have the following advantages over sand castings:

(1) Higher production per unit time per unit of equipment.
(2) Finer grain size and improved mechanical properties.
(3) Closer dimensional tolerances.
(4) Lower costs for machining.
(5) Greater casting yield.

Not all copper-base alloys are well suited to the permanent-mold casting process. The production of castings of intricate shape with either metal or sand cores is usually limited to either the aluminum bronzes or the silicon brasses. The use of tin bronzes and high-lead tin bronzes in this process has proven to be quite successful in the manufacture of bearings and gears simple in design.

Design. In designing a permanent mold considerable care must be made to control the factor of directional solidification. This is readily accomplished in the case of billets or slabs. However, as the casting becomes more intricate in shape, control of the solidification becomes more difficult. The location of cores, the relationship of light and heavy sections to mold partings, and the position of gates and feeding risers are factors that affect the control of directional solidification. The mold should be designed so that heavy sections of the casting are at the mold parting, wherever possible, in order to feed these sections directly from the gate or suitable risers. Because of the high mold cost, it is advantageous to consider all variables before the design leaves the paper stage.

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* "Copper-Base Alloy Foundry Practice," p. 156, American Foundrymen's Society, Chicago, 1952.

Tolerances. Under optimum conditions, castings may be produced within ±0.005 inch variation on a 1-inch section. In ordinary practice, control is usually of the order of 0.01 inch. Tolerance control decreases where heavy mold castings are required.

Mold Material. Basically, mold materials are of two types, castings and forgings. A low-alloy cast iron, with varying amounts of nickel or chromium added to improve the high-temperature properties, has been used with considerable success. The forgings are made from the following types of alloy steels:

(1) Stainless, types 311 and 347
(2) Chrome-vanadium forging steel
(3) Chrome-tungsten die steel
(4) Chrome-molybdenum-vanadium die steel

Cores may be made from either the cast iron or alloy steel. After rough machining, mold sections should be stress-relieved. It is also good practice to heat the finished mold thoroughly before placing it in production as an added precaution against warping and cracking.

Mold Washes. One of the more important phases of the permanent-mold process is the coating of the mold surface with a suitable refractory material. Careful thought must be given to the selection and application of the mold coating, since the quality of the casting, the surface finish and dimensional tolerance, and the life of the mold depend on it. Basically, mold washes consist of a refractory material (clay), a binder (bentonite or water glass), and a lubricant (rouge or graphite) suspended in water and mixed to a consistency suitable for applying with a spray gun. For the successful production of castings from the tin and high-lead tin bronzes, special attention is required in the selection of a proper mold wash to obtain a satisfactory casting finish.

Mold Temperature. Control of the mold temperature is necessary for the production of sound castings. This is rather hard to achieve, but may be obtained by close control of the pouring temperature, by the thicknesses of the mold sections, and by the number of molds being cast per unit time. In general, molds for copper-base casting alloys are held between 120 and 540°C (250 and 1000°F).

Pouring. Various means may be used to reduce the variations in the rates of pouring, such as sumps to control turbulence, chokes in the sprues or runners to slow down the flow of the metal and hold back slag or dross, and vents in the mold walls to reduce the gas pressure in the mold cavity which might cause misruns.

Because of the wide variation of the pouring temperatures of the copper-base casting alloys, it is almost impossible to give any definite information. As in the case of sand castings, the best results are obtained when the lowest possible temperature is used for each alloy. High pouring temperatures lower the rates of solidification and may cause tears and hot cracks. Gas holes and over-all porosity may also result from a high pouring temperature. Also, there is the distinct possibility of decreasing the mold life due to the high temperatures.

Die Casting

Die casting is the art of producing accurately dimensioned castings repeatedly by forcing molten or semi-molten metal under pressure into metal dies. As in the case of permanent-mold casting, the mold or die cost is high and the minimum number of castings that can be made economically is rather high.

The advantages of die casting over other casting processes are (1) they may be made to very close dimensional tolerances, (2) speed of production is very high, and (3) for the production of a large number of castings, the cost per piece is very low.

Dies. Brass die castings may be made with almost the same ease as the zinc, magnesium, or aluminum alloys, but owing to the higher casting temperatures required for the copper-base alloys, the life of the dies is much shorter than the life of the dies used for the alloys of lower melting point. The die steels used for the casting of alloys with casting temperatures up to 700°C (1300°F) are unsuited for copper alloys with casting temperatures up to 925°C (1700°F).

The steel most commonly used for the dies for casting brass is one of the "hot work" steels that are recommended for swaging, forging, extrusion, or other similar methods of fabricating brass. A typical composition of one of these die steels is 3.3 per cent Cr, 0.50 V, and 9.0 W, with 0.30 per cent C, 0.25 Mn, and 0.25 Si.

Die Life. Dies for brass castings may operate from 10,000 to 50,000 cycles before replacement is necessary. The life of the die depends upon the size, weight, and wall thickness of the casting. In some instances, where the casting is small and thin-walled, a die life greatly in excess of 50,000 cycles has been obtained.

Die Design. After the parting line and the general construction of the die have been planned, it is highly important to gate and vent the casting cavity properly. The gates and vents, as thick as can be tolerated, should be placed in their proper positions. In addition, overflow wells, or "pop-offs," should be connected at the vent end of the die and at other points in the cavity where there is the likelihood of trapping air. Gates, vents, and overflow wells have more influence than any other factor in the production of high strength, good surface finish, and soundness in die castings.

The minimum wall section for a brass die casting should be about 0.075 inch with an average of $\frac{1}{16}$ inch for small parts. Uniformity of the wall sections and the avoidance of heavy sections are important in the control of tolerances and soundness. The walls of the brass die castings and any cores used require larger drafts than when die casting the lower melting alloys.

Die Casting Machines. Brass die castings were first produced in a vertical cold-chamber machine introduced by Polak in 1930. They are now also produced on the horizontal cold-chamber machine that is used for the die casting of the lower melting alloys. A description and line drawings of these machines are given in the article, "Casting and Production of Zinc Alloys."*

Alloys. A.S.T.M. Specification B176-50 covers three brass alloys used for die castings. The limits for the composition of these alloys are shown below:

Element	Alloy A	Alloy B	Alloy C
Copper	57.00 min.	63.00 to 67.00	80.60 to 83.00
Silicon	.25 max.	.75 to 1.25	3.75 to 4.25
Lead (max.)	1.50	.25	.15
Tin (max.)	1.50	.25	.25
Manganese (max.)	.25	.15	.15
Aluminum (max.)	.25	.15	.15
Iron (max.)	.25	.15	.15
Magnesium (max.)	—	—	.01
Other elements (max.)	.50	.50	.25
Zinc	30.00 min.	Remainder	Remainder

Alloy A is a general-purpose low-cost brass with wide limits for impurities. Alloy B is an alloy of higher purity having excellent castability and relatively high mechanical properties in the die-cast condition. Alloy C is used where high strength and hardness, coupled with resistance to wear and corrosion, are required.

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* "The Metals Handbook," p. 1078, Am. Soc. for Metals, Cleveland, Ohio, 1948.

The minimum tensile requirements of the alloys shown in the above A.S.T.M. specification are as follows:

Property	Alloy A	Alloy B	Alloy C
Tensile strength, min. psi	45,000	58,000	90,000
Yield strength, 0.2% offset, min. psi	25,000	30,000	30,000
Per cent elongation in 2 inches, min.	10.0	15.0	25.0

Because of the high melting and casting temperatures of other copper-base alloys and the resultant effect on die materials, die casting of these alloys is not economically feasible. However, excellent die castings may be made from aluminum bronzes, tin bronzes, low brasses, and other high-copper alloys if die life is not a factor.

Centrifugal Casting

Centrifugal castings may be classified into three types: true centrifugal, semicentrifugal, and centrifuge castings. According to definition, a centrifuge casting is not a true centrifugal casting, but rather a casting in which centrifugal force is used to provide feeding pressure to a mold cavity outside the axis of rotation. In the true and semicentrifugal processes, the casting is usually symmetrical around the central axis and is spun on this axis during casting.

In true centrifugal casting the axis of rotation may be horizontal or inclined at any angle up to the vertical. The molten metal is poured into the spinning mold and the metal is held against the mold wall by centrifugal force. The outside surface of the casting may be modified from a true circular shape by the addition of flanges or small bosses, but, to secure balance, the shape is generally symmetrical around the axis of rotation. The inside surface of a true centrifugal casting is cylindrical, although a casting made on a vertical machine will generally have a smaller inside diameter at the bottom of the casting, due to gravitational forces as related to centrifugal forces. If correct practices are used, this effect may be held to a minimum and, in any event, may be readily removed by a rough machining operation. Any dross and nonmetallics of low density that may be introduced with the molten metal into the spinning mold move toward the inside surface, where they are removed by the boring operation.

Semicentrifugal castings are similar to true centrifugal castings, except that a central core is used that will allow shapes other than a true cylinder to be produced on the inside surface of the casting. The mold is always spun on a vertical axis in making semicentrifugal castings.

Production Process. The equipment used for producing centrifugal castings basically consists of a shaft suitably mounted in bearings and supporting a face plate or spider to which the mold is fastened. The mold is rotated at speeds that vary with the casting being made and the alloy used. One method in common use to determine speed of rotation is to spin all castings at such a speed as to give a fixed amount of centrifugal force.

Mold Materials. Metal molds, such as cast iron or mild steel, are used where a large quantity of one type of casting is required, making the original cost of the mold justifiable. Graphite molds are used for relatively short-run jobs and offer increased savings over metal molds because of the ease with which graphite may be machined. Dry sand molds are used for the larger castings made in limited quantities, although they have the disadvantage of being used only once.

Uniformity of Product. The uniformity of centrifugal castings compares favorably with that of wrought material, with the further advantage of having nearly equal mechanical properties in all directions as opposed to the directional properties shown in some wrought alloys. When ordinary sections are cast centrifugally, the variation in chemical composition is insignificant for the solid-solution type alloys. There is some variation in composition when the high-lead bronzes are cast and the variation may be increased with greater amounts of lead, heavier sections, and mold materials that allow the metal to cool slowly. In general, the usual composition of any copper-base alloy will not require any modification for centrifugal casting.

Mechanical Properties. The mechanical properties of copper-base alloys cast centrifugally will vary with the alloy composition and to a large extent will depend on the mold material used. Centrifugal castings made in sand molds, where the cooling rate is relatively slow, will have lower mechanical properties than similar castings made in metal or graphite molds. Compared to casting an alloy statically in sand molds, properties averaging 10 per cent and 30 per cent higher may be obtained from centrifugal castings made in sand and chill molds respectively. Comparative properties obtained on a gear ring 36 inches in diameter, 8 inches long, and with a 4-inch wall cast statically in sand and centrifugally in a metal mold are listed below.

Alloy	Method of Casting	T.S., psi	Y.S., psi	Percentage elongation
Aluminum bronze	Static	79,200	28,900	39.8
(88 Cu-9 Al-3 Fe)	Centrifugal	87,600	32,200	40.1
88 Cu-8 Sn-0 Pb-4 Zn	Static	46,700	23,900	24.8
(Navy G)	Centrifugal	51,500	27,100	55.0
Manganese bronze	Static	71,700	26,400	30.3
(65,000 T.S. min.)	Centrifugal	77,500	33,200	37.2

Applications. Probably the largest single use of the centrifugal casting process for copper-base alloys is in the production of bearings or bushings. However, the principal driving force behind the development of centrifugally casting copper-base alloys was the need of the paper industry for large cylindrical castings for use as suction rolls. The centrifugal method is now being used in the production of castings ranging in weight from a few pounds up to 60,000 pounds.

Precision Investment Casting

Precision casting, also known as the "lost wax" or "investment casting" process, is an old method, used for many years in the casting of dental inlays, dentures, and jewelry. New techniques and materials were devised to make it applicable to production methods for intricate shapes used in industry. The process consists of casting a metal or alloy under pressure into a one-piece refractory mold from which a wax or low-melting alloy pattern or cluster of patterns has been removed.

Dimensional Changes. There are four types of dimensional changes to consider in the manufacture of precision castings:

(1) Shrinkage of the wax pattern.
(2) Shrinkage of the metal casting.
(3) Expansion of the investment during setting.
(4) Expansion of the investment during heating.

Generally speaking, for the copper-base alloys, the total shrinkage slightly exceeds the total expansion, and to compensate for this shrinkage the pattern die must be made correspondingly larger than the desired size of the casting.

The casting shrinkage of copper alloys in investment molds varies from 0.5 per cent to approximately 2.0 per cent. Differences in the shape and size of the casting and the nature of the investment have greater effects on shrinkage than any variation in the composition of the alloy.

Tolerances and Sizes of Castings. With careful control it is possible to hold most dimensions within ±0.005 inch per inch. In certain instances, it is often possible to maintain them as close as ±0.002 inch per inch. On small dimensions, such as 0.25 inch or less, tolerances down to ±0.0005 inch have been attained. From the above, it becomes apparent that when designing for precision casting, exact dimensions and allowable tolerances should be given.

The most practical sizes are 3 inches maximum dimension and ½ inch maximum cross-sectional thickness. Minimum dimensions range down to 0.005 inch sectional thickness. Investment molds are usually 5 or 6 inches in diameter and of equal length, accommodating from 1 to 60 pieces, depending on size.

Investments. For copper-base alloys the investment is usually composed of a mixture of fine powdered plaster and silica. This refractory is made fluid with water and poured around the pattern or cluster of patterns in a confining ring or flask. The flask is usually placed under vacuum to prevent the entrapment of air, which would cause defects in the castings. After the investment has set, the molds are heated to between 650 and 760°C (1200 and 1400°F) to melt out the patterns. The alloy may be cast into the hot molds or the molds may be cooled to any desired temperature.

Finish. Many copper-base alloys used for investment casting have a smooth, clean and often bright surface of natural color that needs no further treatment. The surface smoothness compares favorably with that produced by the usual machining methods.

Alloys. Many precision-cast brass parts were previously machined from free-machining yellow brass, naval brass, or other yellow-brass alloys available in rod or extruded shapes. Therefore, an alloy containing 58 to 65 per cent copper, 0.1 to 1.0 per cent aluminum, and the remainder substantially zinc was chosen for precision casting because of its excellent castability and good mechanical properties. For specific requirements, manganese bronzes, aluminum bronzes, and silicon brasses are cast successfully.

Alloys containing over 0.5 per cent lead or high in copper have not been cast successfully, principally due to unsatisfactory surface finish.

Applications. The outstanding feature of the precision investment casting process is its ability to produce parts of intricate shape to accurate dimensions. The process can often provide such features as slots, keyways, blind holes, designs or markings, either raised or depressed, cams, bevels, etc. Often an assembly consisting of many separate parts can be united into a single precision casting with few parting lines, if any.

Plaster Mold Casting

The production of accurately dimensioned castings by the plaster molding process is in most respects similar to the sand foundry method, in that it employs the match-plate system, cope and drag assembly, separately made cores, and gravity pouring. The major difference is the low thermal conductivity of the investment material, which is approximately 1/10 to 1/15 that of green sand molds.

Process. The plaster (calcined gypsum) is usually mixed with various types of fibrous and refractory aggregates, such as asbestos, fibrous talc, clay, graphite, pumice, etc. A typical mixture used for the preparation of plaster molds consists of 70 to 80 per cent plaster of Paris and 30 to 20 per cent fibrous talc. Compositions of this type are generally mixed with a relatively high proportion of water, in the range of 120 to 180 parts of water to 100 parts of the plaster by weight. The slurry thus formed is poured over both the cope and drag halves of the pattern and allowed to set.

The set mold is dehydrated completely to liberate the free and chemically combined water. This dehydration is accomplished by heating the mold in ovens at temperatures ranging from 200 to 760°C (400 to 1400°F) for a period depending upon the size and shape of the mold and the temperature used. At the lower temperature, the length of the heating cycle is generally 24 hours, whereas at the higher temperature the complete cycle may be accomplished in 2 hours. Dehydration of the mold is necessary because the presence of even minute quantities of moisture in the mold at the time of casting would result in the production of imperfect castings.

The process is largely automatic and is continuous in its operation, resulting in fixed time relations in the various stages and allowing maximum control.

Shrinkage. As in the precision casting process, cognizance of the dimensional changes encountered in the setting and dehydrating of the plaster and in the casting of the alloy is necessary if consistent and close tolerances are desired. Generally, the size of the pattern slightly exceeds the size of the finished casting to compensate for the over-all shrinkage.

Tolerances and Sizes of Castings. The control of dimensions depends upon the accuracy of the pattern and on control of the physical factors involved in the process. In general, a tolerance of ±0.005 inch per inch of dimension can be held. Where the dimension crosses a parting line, the tolerance is increased to ±0.010 inch per inch. In specific instances, over-all tolerances of ±0.005 inch for portions within one-half of a mold are being produced commercially. Flatness of surface depends upon casting design. Areas up to 6 square inches may sustain a warpage from 0.007 to 0.015 inch. The smoothness of the surface is also such that in many cases the castings may be electroplated without further polishing.

Most copper-base alloy castings made by the plaster molding process are relatively small in size. Occasionally, certain large castings, that is, about 20 pounds, are made by this method. Since plaster is a poor conductor of heat, the process is ideal for producing thin-walled castings. Wall thicknesses of 0.10 to 0.04 inch, depending on casting design, are being cast commercially.

Alloys. Virtually all the copper-base alloys may be cast in plaster molds; however, on certain alloys special mold surface preparations are necessary, as on leaded red brasses, tin bronzes, and pure copper. The alloys in commercial production are yellow brasses with 0.10 to 1.0 per cent aluminum added, manganese bronze, aluminum bronze, aluminum-silicon bronze, nickel brass with approximately 1.0 per cent aluminum added, and copper-beryllium alloys.

Applications. The principal applications of the plaster molding process are in the production of small, relatively intricate shapes to rather close tolerances, thus saving on machining operations. Among the many types of parts produced by this process are electrical equipment, pump and hydraulic impellers, hardware for railroad and automotive equipment, name plates, bearing retainers, tools, and gears.

OTHER CASTING METHODS

Shell Molding Process

This process, more commonly called the Croning or "C" process, has been one of the most important steps forward in foundry developments in the last decade. In many respects the process is similar to the plaster molding method, where the production of molds could be largely automatic and continuous in its operation, allowing for maximum control. The major difference is that the "C" process uses a clay-free sand of suitable fineness bonded with a thermosetting synthetic resin forming a thin shell around the cope and drag halves of the pattern.

Briefly, the process entails the use of pattern plates heated to about 260°C (500°F). The fine granular sand mixed with a small amount of the thermoplastic is poured into the mold box. The sand-resin mixture forms a soft crust at the pattern interface in 6 to 10 seconds. The excess mixture can then be dumped and used for the next mold half. The soft shell mold still on the pattern plate is heated to 315 to 370°C (600 to 700°F) for 1 to 2 minutes and the hardened shell can then be lifted off the pattern plate. The matching mold halves are clamped together, backed up by metal shot, and poured in the usual manner. The investment (sand-resin mix) is destroyed during shakeout, but the metal shot is reclaimed for reuse.

Cores are made in a similar manner, the investment generally being blown into a heated core box, the excess mold material being slushed out to provide a thin hollow core.

Some of the advantages of this process over sand casting include (a) stability of molds and cores with respect to volume change; (b) exceptional mold smoothness with a high degree of gas permeability; (c) molds may be stored for indefinite long periods without damage;

(d) increased mold production for a given floor area and labor force; (e) production of castings to true dimensions with exceptional detail and finish.

Vacuum Die Casting

This process entails practices encountered in both the die-casting and permanent-mold processes. The method of filling the mold is similar to the "goose neck" die-casting machine, with the die practice similar to that used for permanent molds.

The sprue opening of the die is submerged in a pot of molten metal and through it the molten metal enters the mold cavity. Vacuum is then applied through the vacuum outlet in the die, creating a differential in pressure between the mold cavity and the atmospheric pressure on the molten metal in the pot. This differential in pressure causes the molten metal to flow into the die and fill the cavity completely. By controlling the vacuum, the pressure differential between the cavity and the molten metal can be varied. This results in very close control of the rate of fill of the die cavity.

In regard to tolerances, shrinkage, applications, and sizes of castings, the vacuum die-cast process is similar in most respects to the permanent-mold process.

Copper-base alloys used in this process have been limited in production to the aluminum bronzes and silicon brass, principally because of inferior surface finishes obtained on other copper-base alloys. The basic advantages of this process over the gravity pouring of permanent molds are the increased soundness and slightly higher properties obtained, due to the close control over the rate of fill of the mold cavity. Also, by submerging the sprue opening beneath the surface of the molten metal, only clean metal free of oxides and dross enters the mold cavity.

COMPARISON OF CASTING METHODS

Table 27-1 shows the various factors involved in a comparison of casting methods for copper-base alloys. These factors are rated 1 through 6, the number 1 being the most advantageous and 6 the least. The evaluation is based upon castings in the as-cast state and may help the engineer to determine which of the casting methods is most advantageous in the ultimate use of the product.

The table is based on casting sizes up to a maximum that can be produced practically in a 12 by 18 by 4-inch mold or the equivalent die size required to produce a casting of similar size in the die-casting, permanent-mold, or lost-wax processes.

TABLE 27-1. COMPARISON OF CASTING METHODS FOR COPPER-BASE ALLOYS

Factor	Sand Cast	Permanent Mold	Die Cast	Lost Wax	Plaster Mold	"C" Process
Tolerances	6	4	3	1	2	5
Surface finish	6	5	3	1	1	3
Thickness of section[a]	6	5	3	1	2	4
Structural density	4	1	3	2	5	4
Pattern or die cost	1	5	6	4	2	3
Speed of getting into production	1	5	6	4	2	3
Speed of production	2	3	1	6	5	4
Cost per piece[b]	2	3	1	6	5	4
Flexibility as to alloys[c]	1	5	6	3	4	2
Low casting stresses	4	5	6	2	1	3
Flexibility of design	2	6	5	1	3	4
Limitation of size[d]	1	2	6	5	4	3
Reproducibility[e]	6	5	4	1	2	3
Pressure tightness[f]	1	6	5	3	4	2

[a] Minimum section.
[b] Large quantity.
[c] Actual production.
[d] Maximum size.
[e] As to dimensions, surface finish, uniformity of properties for successive castings.
[f] According to common usage for pressure castings.

1—Most advantageous
6—Least advantageous

Chapter 28

Hot Working of Copper and Copper Alloys

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Hot working, *i.e.*, elastic and plastic deformation above the recrystallization temperature, is the first step in the fabrication of the major percentage of all copper and copper alloys because it is usually the most economical method of reducing the cross section for further fabrication or forming finished shapes where possible.

Hot working, as defined, results in no work hardening in copper or copper alloys when cooled to room temperature. However, some phase changes occur during hot working; also some constituents undergo thermal transformation by cooling conditions and these may produce measurable hardening, but true hot working differs from cold working in that hot-worked metal is substantially free from the strain-hardening effects of cold-worked metal.

The distortion of the lattice crystal structure and consequent work hardening by cold working has been theoretically analyzed and explained by the study of slip planes in single crystals and also to some extent in the more complex movements of polycrystalline metal. However, there is little information, because of the difficulty of experimental manipulation, regarding the exact physical movement or changes that occur under normal hot-working conditions, except that large deformations can be carried out with much less power and without any significant work hardening.

The quality of the finished products, assuming that the cast shape has the desired analysis and is sound and of good surface, is influenced to a considerable extent by the quality of the hot-rolled rod, bar, slab, etc. It is seldom economical, and in some cases impossible, to eliminate satisfactorily by subsequent operations physical defects or unsatisfactory microstructure that may be produced in hot working. Therefore, the design of all handling, heating, and hot-working equipment, as well as control of operations, is of prime importance in the production of high-quality products.

The fundamental design of the mechanical equipment is similar to that used for other metals, but many details are based upon the results of experience, because the practical knowledge, gained by many years of development in learning how to obtain the desired results without knowing exactly why, is still, in many instances, in advance of theory.

There are many publications describing the theoretical factors involved in the design of certain equipment such as flat rolls[1], but the deformations that take place in rolling or extruding irregular sections are so complicated that the design of such equipment may be described as an art rather than a science, and it will probably remain so for a long while.

Copper and most of its commercially important alloys can be hot worked by one or more of the following methods: rolling, extruding, piercing, forging and pressing, or bending and forming.

The ability of copper and its alloys to withstand plastic deformation above their respective recrystallization temperatures without cracking is the usual criterion upon which their relative suitability for hot working by these methods is judged. Metal which cracks excessively is called hot short and considered unfit for hot working.

Copper and most of the metals, such as zinc, nickel, aluminum, etc., used in making commercial alloys can be procured in a high degree of purity. However, the minor constituents or impurities are an important factor affecting the hot-working characteristics of both copper and its alloys. The principal reason for this is that small quantities of certain elements or intermetallic compounds, present as impurities or added to some alloys, form a brittle phase of low melting point that segregates, during solidification of the casting, at the grain boundaries and lowers the cohesive force between the crystals of the major constituent. Consequently, metal weakened by the presence of such a phase is either unsuitable or limited to certain methods of hot working.

Some methods require the metal to withstand more severe tearing or elongating stress than others, *viz.*, piercing *vs.* rolling, and the inherent characteristics of some methods and equipment are more prone to produce certain physical defects or undesired microstructure. Therefore, the choice of method used depends to a large extent upon the specification of the finished metal as well as the ability of the metal to withstand the alternate methods that may be available.

The relative suitability of the various commercial coppers and copper alloys for the usual hot-working operations is shown in Table 28-1, in conjunction with their nominal compositions.

TABLE 28-1. CLASSIFICATION OF COPPER AND COPPER ALLOYS ACCORDING TO HOT-WORKING CHARACTERISTICS[a]

Metal	Nominal Composition				Hot-Working Operations				
	Cu	Zn	Sn	Pb	Rolling	Extrusion	Piercing	Forging and Pressing	Bending and Forming
Electrolytic copper	99.92	—	—	—	E	G	E	G	E
Deoxidized copper	99.94	—	—	—	E	G	E	G	E
Leaded copper	99.0	—	—	1.0	P	F	P	P	P
Gilding metal, 95%	95.0	5.0	—	—	E	G	G	G	G
Commercial bronze, 90%	90.0	10.0	—	—	E	G	G	G	G
Red brass, 85%	85.0	15.0	—	—	E	G	G	F	F
Low brass, 80%	80.0	20.0	—	—	E	G	F	F	F
Cartridge brass, 70%	70.0	30.0	—	—	G	G	G	G	G
Yellow brass	65.0	35.0	—	—	F	G	F	P	F
Muntz metal	60.0	40.0	—	—	E	E	E	E	E
Leaded commercial bronze	89.0	9.25	—	1.75	P	F	P	P	P
Low-leaded brass (tube)	67.0	32.5	—	0.5	P	G	P	P	F
Low-leaded brass	64.5	35.0	—	0.5	P	F	P	P	F
Medium-leaded brass	64.5	34.5	—	1.0	P	F	P	P	P
High-leaded brass (tube)	67.0	31.4	—	1.6	P	F	P	P	P
High-leaded brass	62.5	35.75	—	1.75	P	G	P	P	P
Extra high-leaded brass	62.5	35.0	—	2.5	P	F	P	P	P
Free-cutting brass	61.5	35.5	—	3.0	P	E	P	P	P
Leaded Muntz metal	60.0	39.5	—	0.5	G	E	F	E	G
Free-cutting Muntz metal	60.5	38.4	—	1.1	G	E	F	E	G
Forging brass	60.0	38.0	—	2.0	F	E	F	E	G
Architectural bronze	57.0	40.0	—	3.0	P	E	P	E	G
Admiralty metal	71.0	28.0	1.0	—	F	G	P	P	F
Naval brass	60.0	39.25	0.75	—	E	E	E	E	E
Leaded naval brass	60.0	37.5	0.75	1.75	F	E	F	G	G
Phosphor bronze, 5% (A)	95.0	—	5.0	—	P	P	P	P	P
Phosphor bronze, 8% (C)	92.0	—	8.0	—	P	P	P	P	P
Phosphor bronze, 10% (D)	90.0	—	10.0	—	P	P	P	P	P
Phosphor bronze, 1.25% (E)	98.75	—	1.25	—	G	F	P	F	F
				Fe					
Manganese bronze, (A)[a]	58.5	39.2	1.0	1.0	E	E	P	E	E

[a] Normally, 0.3% Mn is found in the (A) bronze and 3.7% Mn in the (B) bronze.

Table 28-1. Classification of Copper and Copper Alloys According to Hot-working Characteristics[a] (*Cont'd*)

Metal	Nominal Composition Cu	Zn	Sn	Pb	Hot-Working Operations Rolling	Extrusion	Piercing	Forging and Pressing	Bending and Forming
			Al	Fe					
Manganese bronze, (B)[a]	65.5	23.3	4.5	3.0	G	E	P	G	G
Aluminum brass	76.0	22.0	2.0	—	G	G	F	F	F
Aluminum bronze, 5%	95.0	—	5.0	—	G	F	G	F	G
Aluminum bronze, 8%	92.0	—	8.0	—	G	G	G	G	G
Aluminum bronze[b]	89.5	—	9.0	1.0	F	G	F	G	G
Aluminum bronze[c]	87.0	—	10.0	3.0	F	G	F	G	G
			Ni	Pb					
Nickel silver, 10%, leaded	45.0	42.5	10.0	2.5	P	G	P	G	G
Nickel silver, 18% (A)	65.0	17.0	18.0	—	F	P	P	P	P
Nickel silver, 18% (B)	55.0	27.0	18.0	—	F	P	P	P	P
Cupro-nickel, 20%	80.0	—	20.0	—	G	G	P	F	G
Cupro-nickel, 30%	70.0	—	30.0	—	G	G	P	F	G
				Si					
High-silicon bronze, (A)[b]	96.0	—	—	3.0	G	F	P	G	G
Low-silicon bronze, (B)e	97.7	—	—	1.5	G	G	P	G	G

[a] *Normally, 0.3% Mn is found in the (A) bronze and 3.7% Mn in the (B) bronze.*

[b] Other additions, including Sn, Ni, and Mn may be present to a total of 2.25%.

[c] This alloy is susceptible to heat treatment.

[d] One of the following elements—Fe, Zn, Mn, Sn—may also be present in the alloy to about 1%.

e One of the following elements—Fe, Zn, Mn, Sn—may also be present in the alloy to about 0.8%.

EXPLANATION OF CODE LETTERS USED IN CLASSIFICATION:

E	Excellent	Capable of sustaining very severe total working, at high rates, within a relatively wide range of temperature, showing substantial freedom from hot shortness, consuming low power input, having a low rate of wear on dies and rolls, and using commercial equipment generally available.
G	Good	Somewhat less amenable to working with respect to one or more of the factors under Excellent, but still economically feasible.
F	Fair	Decidedly less amenable to working with respect to one and usually more of the factors enumerated under Excellent, and of questionable or marginal economy.
P	Poor	Either impossible to work, or so deficient in at least one of the factors under Excellent, that the operation is not practicable.

Working Temperature and Its Effect

There is a limited temperature range within which the metal or alloy has the optimum characteristics for specific hot-working methods and equipment.

Suitable temperatures for the various alloys and methods are given in Tables 28-2 through 28-5.

TABLE 28-2. HOT-ROLLING TEMPERATURES[2]

Metal[a]	Copper, Per Cent	Initial Hot-Rolling Temperature, deg. Fahr.	Properties as Hot Rolled[b] Tensile Strength, psi	Percentage Elongation in 2 inches
Electrolytic copper	99.92	1300 to 1600	33,000	50
Deoxidized copper	99.95	1300 to 1600	33,000	50
Gilding metal	95.0	1400 to 1600	36,000	45
Commercial bronze	90.0	1400 to 1600	36,000	50
Red brass	85.0	1450 to 1650	40,000	50
Low brass	80.0	1450 to 1600	45,000	55
Cartridge brass	70.0	1350 to 1500	48,000	55
Muntz metal	60.0	1250 to 1450	55,000	50
Naval brass	62	1250 to 1450	55,000	45
Phosphor bronze, 1.25% (E)	98.7	1450 to 1600	40,000	45
High-silicon bronze (A)	96.0	1350 to 1550	55,000	60
Low-silicon bronze (B)	97.7	1350 to 1550	40,000	50

[a] See Table 28-1 for nominal compositions of these metals.
[b] The mechanical properties shown are average and are not to be used as minimum requirements.

The temperatures shown in Tables 28-2 through 28-5 have been determined mainly by experience, as no scientific laws or rules have been developed.

Forging, compression, bending, tensile strength, and other tests in which a new alloy is compared to an existing alloy at elevated temperatures, are used to furnish indicative information for estimating power requirements and general suitability for the alternate methods of hot working[27, 28], but only through production experience can the tendency to crack in rolling, piercing, or extrusion be obtained.

Practically all hot-worked copper and copper alloys are heated in oil or gas-fired furnaces as these fuels usually permit the most economical combination of temperature and atmosphere control.

The tunnel-type furnace using combustion gases as an atmosphere and fitted with continuous metal feed and discharge is in general use. This type of furnace is usually operated with a neutral to slightly reducing atmosphere to prevent the formation of too heavy an oxide scale, or deoxidizing and embrittling electrolytic tough-pitch copper with reducing gases.

Soaking or homogenizing heat treatment before hot rolling is practiced to only a limited extent with copper alloys. In fact, prolonged heating or excessively high temperatures are to be avoided in most cases as these conditions are favorable to such results as the formation of heavy surface scale, changing the surface composition of certain alloys, *viz.*, dezincing the surface of brass and coalescing the copper oxide in the $Cu:Cu_2O$ eutectic present between the copper crystals of electrolytic copper. The latter is particularly deleterious as it causes unsatisfactory performance in subsequent operation or defects in the finished metal. Copper oxide coalesced in heating for hot rolling will cause excessive breaks in drawing wire and pinholes in thin sheet or strip. However, some very important phase changes occur by reason of the normal heating and hot-working operations.

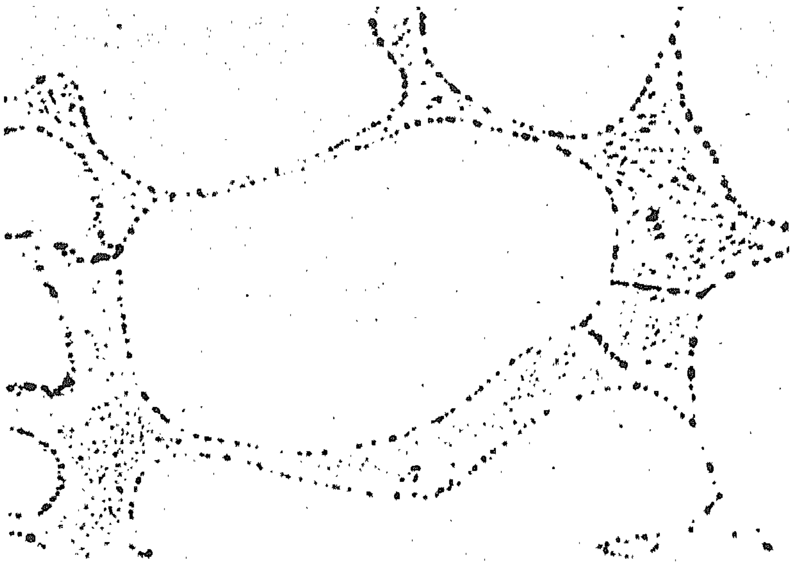


FIGURE 28-1. Microstructure of tough-pitch electrolytic copper as cast, showing Cu-Cu_2O eutectic between large grains of pure Cu. Magnification 750X.

Because of rapid cooling a large tonnage of alpha brass is produced from castings containing a varying amount of the beta phase. During heating and hot working the beta phase, usually present in alloys of approximately 65 to 70 per cent copper, is absorbed by the higher copper-content alpha, producing a homogenized single-phase alpha alloy.

Also in hot working electrolytic copper, the relatively large crystals of copper and the eutectic between them are strained and fractured; recrystallization of the copper from new nuclei proceeds immediately. During this process the eutectic disappears as such, the fine copper particles of the eutectic being absorbed by the copper crystals in the immediate vicinity or coalesced into new copper crystals. This leaves the Cu_2O particles from the eutectic distributed throughout the metal. The result of this phenomenon is illustrated in Figure 28-1, showing the microstructure of cast electrolytic copper containing approximately 0.04 per cent oxygen, and Figure 28-2 showing the same metal after hot working.

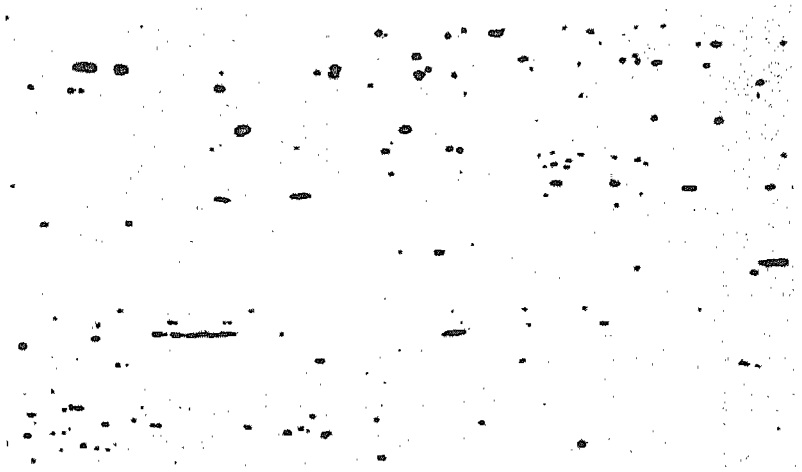


FIGURE 28-2. The same metal as in Figure 28-1 after hot working. Magnification 750X.

Sulfur in cast copper is present as a Cu-Cu_2S eutectic that also disappears as such in hot working. The resulting particles of Cu_2O and Cu_2S have the same appearance when viewed under a microscope with ordinary illumination, but can be distinguished from each other under polarized illumination because the Cu_2O particles are, under this illumination, ruby red and the Cu_2S black.

The eutectic of cast copper and the cuprous oxide content of the hot-worked product are generally referred to in the literature and materials specifications in terms of oxygen, which is the same in both samples, but it is more descriptive to refer to the casting as containing approximately 10 per cent Cu-Cu_2O eutectic and the hot-worked metal as containing approximately 0.37 per cent cuprous oxide.

The change in the oxide phase during hot working improves the physical properties of copper but reduces the accuracy of microscopic oxygen estimation.

Oxygen-free and deoxidized copper contain no copper oxide eutectic. However, all commercial copper contains a small amount of sulfur, averaging about 0.0015 per cent. This sulfur is present as cuprous sulfide that forms a eutectic similar to the oxide and, as noted, changes phase in the same manner.

Other minor constituents may change phase depending upon the hot-working temperature. For instance, the solid solubility of lead in oxygen-free copper is about 0.04 per cent at the usual hot-working temperature, *i.e.*, 800°C (1475°F), and approximately 0.003 per cent at 600°C (1110°F). Therefore, a substantial portion of the lead may precipitate during the actual hot working or upon slow cooling. Likewise arsenic and antimony may behave in a similar manner.

A more detailed discussion of changes in solid solubility may more properly be presented under the subject of Heat Treatment. However, it has been found desirable to a very limited extent to make use of the change in solubility of some minor constituents by controlling the hot-working temperature and quenching the metal to prevent precipitation of certain minor constituents because of their effect on recrystallization temperature. In general, hot working in a temperature range to insure the maximum solubility of the minor constituents results in less cracking, and when followed by rapid quenching results in the highest possible recrystallization temperature of the finished products. Copper wire cold drawn after such a hot-working procedure will withstand higher temperature without softening, for longer periods of time.

Density and Its Effects

The density of practically all hot-worked copper and copper-alloy products is higher than the castings from which they are made because the shrinkage and gas cavities or porosity present in varying amounts in commercial castings are reduced in volume by compression in working. In general copper and high-copper alloys are increased most because their castings are usually less dense. However, continuous-cast copper and copper alloys are an exception, as these castings are particularly dense. The density of continuous-cast phosphorus-deoxidized copper is 8.95 grams per cc. At the other extreme the density of the cold-pressed billets used in the production of oxygen-free coalesced copper is increased during extrusion from an apparent density of 7.7 to 8.93 grams per cc, or 15 per cent.

While the coalesced-copper process[3] is in limited use, it is of particular interest in connection with hot working because of the basic metallurgical factors involved.

In the coalesced-copper process irregular shaped pieces of metal, produced by breaking brittle electrolytic cathodes, varying in size from very fine particles to pieces approximately ¼ inch thick and several square inches in area, are cold pressed, instead of cast, into billets of suitable size to enter standard extrusion press containers. These billets are heated to 870 to 925°C (1600 to 1700°F) in a deoxidizing and desulfurizing atmosphere of steam and city gas, *i.e.*, gas containing hydrogen and carbon monoxide, and transferred to an extrusion press container under the same atmosphere.

During extrusion the gas is squeezed from the space between the pieces and thus largely eliminated. Simultaneously the copper crystals are strained or fractured and recrystallized by the high temperature from many new nuclei growing in all directions by absorbing heavily strained or fragmented crystals from their immediate vicinity. This results in a complete rearrangement and intergrowth of crystals from the original pieces and consequently the same crystal structure and physical properties in the extruded metal as would be obtained from a cast oxygen-free billet.

Since the spaces between the pieces of metal in the pressed billets are connected, the gas therein can flow and escape during extrusion, resulting in a relatively large increase in density and sound metal.

In castings, gas and shrinkage cavities are entirely surrounded by metal having no connecting path to the outside. These are only partially eliminated during any method of hot working.

Some cavities are eliminated as the normal flow of the metal during working brings them to the surface, where they are broken open, allowing the gas to escape and the metal to make intimate contact and coalesce through further working, or the resulting slivers are scaled off by oxidation.

The outer wall of gas cavities becomes thinner as hot working progresses and in some instances the high pressure of the confined gas is great enough to expand the thin wall and form blisters immediately after the metal leaves the rolls or dies.

However, if blisters formed from gas cavities open on the last pass so there is no further hot working, the surface will be defective. Defects of this type are known as "spills" or "slivers."

Likewise any incompletely adhering film of metal on the surface is commonly called "spill."

Spilly surface metal may also result from defects or inclusions in the surface of the castings, such as cold shuts, slag, mold wash, etc. Casting defects of this type are the result of poor casting or inspection procedure and the methods used to limit or prevent the production or delivery of such castings to the hot-working mills have been described in a previous chapter and the literature[4].

It is quite evident that there is some critical size with respect to *cavities and the resulting surface quality* of the hot-worked products. Electrolytic copper and some high-copper alloy castings contain many cavities of microscopic size. These do not produce slivers and blisters of objectionable size or alter to any marked extent the physical properties of the hot-rolled products. On the other hand, cavities above some particular size do produce commercially defective metal as described above. It is believed that the location of the gas cavities in the castings determines the critical size above which surface-defective material will be produced.

Crystal Structure

Many copper and copper-alloy castings have a microstructure composed of a wide zone of large primary crystals or dendrites extending *from a thin layer of smaller crystals on the outer surface to or near the* middle. The boundaries where these large columnar crystals meet from opposite and adjacent sides form planes of weakness. The presence of this type of macrostructure has an important bearing on the design of the cast shape, such as the radius used on the corners of rectangular bars for flat rolling and the design of the initial rolling passes in rod mills.

Examples illustrating the effect of macrostructure on cracks in hot working are: (1) hot rolling a rectangular copper cake 4 inches thick and having a 2-inch radius on the sides; *i.e.*, a semicircular edge entering at 90° to the face of the rolls may crack severely, whereas the same metal or alloy and the same dimensional cake having flat sides with ¾-inch radius on the fillets may not crack at all. Likewise standard-size copper or copper-alloy wirebars (approximately 4½ by 4½ by 52 inches *long) having ¾-inch radius fillets may crack severely if rolled on flat* rolls or box passes in bar mills, and with little or no cracking if rolled in a gothic or other grooved pass that confines the metal at the filleted corners. The dendritic macrostructure of most round billets is also one of the reasons that precludes their successful or economic rolling on flat rolls.

There are no laws or fixed rules to determine the most advantageous dimensions of slab, cake, or bar design with respect to hot working with a minimum of cracking, but experience has shown the general advisability of avoiding too large a radius or a sharp 90° corner. A radius of ½ to ¾ inch on corner fillets is generally most satisfactory.

Dimensions other than the radius of fillets are also of importance, as they are a controlling factor in the mold design and other casting details that have an indirect effect on hot working, in that certain dimensional relationships of the castings result in incipient or very fine and shallow cracks on the surface of the castings that open and tear in hot working.

The extent of cracking in hot rolling copper and its alloys, resulting from cracks in the surface of castings, is not easily determined and in many cases the casting conditions cannot be adjusted to eliminate them completely.

Fundamentally, cracks in the surface of castings are caused by shrinkage during solidification that results in internal stress or friction on the mold surface because of movement in the mold. A full discussion of this problem is not presented here as it is more pertinent to the subject of casting, but the following will serve as an example of each type and is indicative of the problems to be overcome in correlating the dimensions and consequently the weight of the casting, with the mold design, casting procedure, and desired hot-worked product.

During solidification some castings crack on the surface from internal pressure caused by solidified metal contracting around a liquid core, thereby raising the internal pressure above the bursting strength of the surrounding shells, or from the increase in pressure from gas being liberated from the liquid core. In the case of electrolytic copper the liquid core becomes richer in eutectic, which will run out and solidify on the surface of the casting forming the well-known exudation commonly called sweat. This condition can be controlled to a considerable extent by coordinating the dimensions of the casting, the mold design, and mold dressing so that the cooling rate and pattern of heat flow from the metal to the mold allow the metal to solidify in a pattern that permits the top to remain liquid or yield to internal pressure until the side walls have become sufficiently thick to withstand the internal pressure without cracking.

Exudations are also common on silicon and tin bronze castings.

It is common practice to chip off exudations; however, cakes or slabs for flat rolling will frequently crack at these places during hot rolling and sometimes produce surface defects.

Cracks produced by mold friction are frequently the result of mold warpage, irregularities in mold walls that prevent free movement, excessive length, or from inherent weakness of the macrostructure of the metal or alloy at temperatures near their melting point. This type of crack may vary in size from an almost visually obscure line between a few macrocrystals on the surface to an opening that is plainly visible and extending for inches in length.

In some cases, castings having minor surface cracks can be processed to produce perfectly satisfactory hot-worked products. This is particularly true where they are to be extruded, but in other operations, such as rolling where tensile stress may be applied during processing, the cracks become larger and often result in defective products.

Composition—General

The chemical and physical composition of the various grades of copper and its alloys is one of the most important factors that determines their suitability for hot rolling, piercing, extrusion, etc.

The effect of the basic components, such as variation in the percentage of copper and zinc in brass, aluminum and copper in aluminum bronze, etc., on the working characteristics has been determined by numerous research investigators and their results are in general agreement with industrial experience. There is also good agreement regarding the general effect of the additives such as lead to brass, phosphorus to copper, etc. However, this agreement does not exist in the experimental results reported in the literature or the experience of industrial workers with respect to the effect of minor constituents or impurities.

It is pertinent to refer to the effect of the configuration and size of the casting and note that some of the discrepancies in results are most probably due to the castings used for the investigations.

Small, well-cast laboratory or furnace-charge sample castings having a uniform and fine grain can usually be hot worked over a wider temperature range with less cracking than commercial-size castings made from the same furnace charge. This is particularly true with respect to electrolytic copper, which is sensitive to small variations in impurity content. The sum total of all impurities in electrolytic copper other than oxygen is usually less than 0.01 per cent, the individual metals each being under 0.002 per cent.

Commercially cast electrolytic wirebars of approximately one-half standard size, *i.e.*, 135 to 175 pounds, cast from the same furnace charge as standard 250-pound bars, have often been observed to hot roll with little or no cracking while rather severe cracking occurred on the standard-size bars.

Observations such as this and others of a similar character are most probably responsible for the difference in opinion regarding the limits of impurities that may be tolerated in commercial hot processing of both copper and its alloys.

Other factors that further complicate the setting of definite limits for impurities are that the presence of some impurities has an appreciable effect on others; for instance, the presence or absence of cuprous oxide eutectic in cast copper determines the limiting concentration of lead, bismuth, and other impurities that can be tolerated for commercial hot rolling. Also, the lateral flow, and consequently the stress relationships at the edges of rolled slabs, change with variations in rolling practice. Heavy reductions in the early passes cause more lateral flow and generally produce bulging rounded edges while light reductions per pass may produce concave edges, the effect of both being changed where edging rolls are used.

In general it can be said that the most pure copper can be hot worked with the least cracking, and that there are no definite limits for each deleterious impurity below which one can be assured there will be no cracking. The tendency to crack increases with impurity concentration, the maximum amounts permissible for good commercial results varying with the type of hot-working process and products desired.

From the following discussion concerning the effects of composition and impurities, and for the purpose of simplification, certain general statements can be made with few if any exceptions.

(1) The hot-working properties of pure copper and its commercial alpha alloys are adversely affected by the presence of small quantities of lead and bismuth and it is desirable to maintain other impurities at as low a level as is commercially practical.

(2) The commercial beta and alpha-plus-beta copper alloys have better hot-working properties and can tolerate without adverse effect a higher concentration of lead and other impurities than the alpha phase of the same series.

(3) Cracking is more prevalent in hot rolling and piercing than in other hot-working processes and consequently castings intended for these operations must be more pure and physically perfect than is usually necessary for extrusion.

Effect of Composition on Hot Working of Copper

Metal containing over 99 per cent copper is generally referred to as copper, but a prefix is used whenever a small amount of another element has been added; examples are: silver-bearing copper[16] that contains from 7 to 25 oz Ag per ton; phosphorized copper, containing 0.005 to 0.035 per cent P; silicon copper containing up to 0.5 per cent Si; arsenical copper, 0.3 to 0.5 per cent As; tellurium copper up to approximately 0.75 per cent Te; cadmium copper up to approximately 1 per cent Cd; chromium copper up to approximately 1 per cent Cr; and possibly others.

Commercially pure coppers with a minimum of 99.9 per cent Cu and having an electrical resistivity not exceeding 0.15328 ohm per meter-gram are called high-conductivity coppers, and include oxygen-bearing (commonly called tough-pitch or electrolytic) and all oxygen-free such as the carbon-deoxidized OFHC brand or deoxidized copper having a small but limited amount of residual deoxidizer.

Copper containing less than 99.9 per cent copper, or having a specific resistivity higher than 0.15328 ohm per meter-gram, is called casting or fire-refined copper. Such metal is derived from either secondary sources or from primary sources where the precious metals contents are too low to justify electrolytic refining.

All of the "coppers" can be easily hot worked within the temperature range of 800 to 900°C (1420 to 1650°F) by any of the standard methods and equipment. However, high-conductivity metal is usually hot rolled at 650 to 750°C (1200 to 1380°F), as less surface oxidation occurs in heating the cake and consequently sheets and strips of better surface quality are produced within this range.

Cadmium copper is generally rolled at a lower temperature[5] or deliberately allowed to cool after the heavy breakdown reductions in order to finish with a slightly cold-worked product having higher tensile strength than would otherwise be produced.

Chromium and tough-pitch arsenical coppers are usually rolled in the higher temperature range[5] (800 to 900°C, 1470 to 1650°F), because chromium copper may age harden during rolling if allowed to cool below approximately 700°C (1290°F) and tough-pitch arsenical has a brittle range between 600 and 700°C (1110 to 1290°F). Both of these metals have a greater tendency to crack at any temperature than high-conductivity copper, but are commercially hot worked by careful processing.

The oxygen content of cast electrolytic, fire-refined, and tough-pitch arsenical coppers varies between 0.015 and 0.05 per cent, and within this range has in itself no deleterious effect on hot working[6]. However, its presence changes the chemical form and solubility of other elements that may be present and in so doing affects the hot-working characteristics, particularly rolling and piercing.

The degree of embrittlement produced by arsenic varies with the cuprous oxide content[7, 16], metal having a high ratio of oxygen to arsenic content being the most brittle, low arsenic (0.05 per cent) with high oxygen (0.05 per cent or more) being most difficult to hot roll.

The embrittling effect of lead[8], bismuth[9], and antimony[10] is also influenced by the oxygen content, the maximum amount permissible being increased by the presence of oxygen.

These elements, as well as iron[11], nickel, sulfur[12], selenium, and tellurium[13, 14, 15], have no commercially significant effect on hot working within the limits present in standard electrolytic copper regardless of the presence or absence of oxygen. However, fire-refined copper may contain a much greater amount of one or more of these elements and consequently may crack in hot working.

Although cuprous oxide increases the percentage of most impurities permissible for good hot working, it is impractical to go beyond the maximum amount (approximately 0.05 per cent oxygen) present in commercial copper because it lowers the ductility of the finished products.

Copper-Zinc Alloys

All commercial copper-zinc alloys ranging from 54 to 97 per cent copper are hot worked by one or more of the standard processes.

The beta alloys containing 54 to 56 per cent copper and the duplex alpha-plus-beta alloys containing 56 to 62 per cent copper are some of the most easily worked copper alloys. However, most of the duplex and all of the beta alloys are extruded.

The hot working of the alpha alloys, those over 62 per cent copper, to produce sheet, strip, tube, rod, and extruded shapes has been increasing steadily since high-purity (low-lead) zinc became commercially available. One of the reasons for this is that these alloys become hot short if contaminated with very small quantities of certain metals, such as lead and bismuth.

Difficulty is rarely experienced in hot working alpha brass produced from high-purity copper and zinc, but economic necessity requires the use of some remelted mill and fabrication scrap that may result in slight contamination. Therefore, all mills have established arbitrary maximum limits on lead and other impurities based on their particular operations and experience.

As with copper there is diversity of opinion regarding the maximum limits of impurities that can be tolerated and for essentially the same reasons.

Lead has been shown by many investigators[17, 18, 19], and by practical experience, to be one of the most deleterious impurities in alpha brass, and it is generally agreed that the maximum amount that can be commercially tolerated is approximately 0.02 per cent. With accurate temperature and processing control it may be possible to slightly exceed this amount. However, it is customary for mills to establish lower limits in order to obtain a working margin in their operations. Many mills limit lead in the alpha alloys intended for hot rolling to a maximum of 0.015 per cent or less. A higher maximum lead content is permissible in the alpha brasses intended for extrusion, the usual limit being approximately 0.05 per cent.

Very small quantities of bismuth[20] also make the alpha brasses hot short, a few thousands of 1 per cent having a marked effect.

Arsenic, antimony, or phosphorus is sometimes added to brass as an inhibitor to dezincification. These elements in the amount used (approximately 0.05 per cent) have no noticeable effect on hot working, particularly as most of this type of metal is extruded for tubes.

The limits for iron in copper-zinc alloys are usually determined by its effect on grain size and other characteristics of the desired finished products, and for these reasons are usually limited in alpha alloys to approximately 0.05 per cent. Other nonleaded alloys containing much more iron, such as high-tensile brass containing 1 per cent iron, have good hot-working characteristics over a wide range of temperature.

Iron and aluminum offset some of the embrittling effect of lead[21]. One per cent lead in 60-40 brass will cause severe edge cracking in otherwise pure 60-40 brass, but the addition of 1 per cent iron to the same alloy will considerably reduce this effect.

The general use of pure copper and zinc in making brass has resulted in such small quantities of other impurities being present, such as selenium, tellurium, sulfur, etc., that their effects on commercial hot working are considered inconsequential, and therefore have been given little systematic investigation. There is little change in resistance to deformation at elevated temperature by variations in composition of the numerous copper-zinc alloys, therefore, no changes in mechanical equipment or sequence of reductions are necessary, although the preheat temperature is varied to obtain optimum results. Commercial preheat working temperatures vary between approximately 650 and 850°C (1200 to 1560°F), depending upon the composition of the brass, whether it is to be rolled, pierced, or extruded, and the physical properties of the desired end products. Usually a higher temperature is used on the alloys of higher copper content.

Copper-Nickel Alloys

All of the binary alloys of copper-nickel known as cupro-nickel containing from 4 to 30 per cent nickel are hot worked by rolling and extrusion; however, they require closer temperature control and more power than pure copper.

These alloys, like copper and alpha brass, are embrittled by small quantities of lead and bismuth and other impurities, the commercial maximum limit for lead being approximately 0.05 per cent or less.

Bismuth contamination is avoided by the use of high-purity copper and nickel, with the result that this element is usually present in amounts less than 0.001 per cent in commercial practice.

Small quantities of sulfur of the order of 0.01 per cent or less are known to make nickel unworkable because of the presence of a Ni-Ni_3S_2 eutectic of relatively low melting point, 644°C (1190°F), that segregates at the grain boundaries. Manganese is added to convert this to manganese sulfide, which separates as small globules having no embrittling effect in hot working.

It is also general practice to add manganese to the copper-nickel alloys for the same reason, and in addition these alloys are usually carefully deoxidized with magnesium.

Magnesium is usually added in sufficient quantity to deoxidize the metal, leaving only a trace in excess, but manganese may be added in excess from 0.01 to several per cent as an alloy constituent.

Sulfur and oxygen present no commercial hot-working problems with these alloys because of the general practice of using only high-purity copper and the addition of manganese and magnesium.

Carbon is an impurity that may be present from the use of greasy mill scrap or other contamination in melting, and is limited to approximately 0.05 per cent or less because of its adverse effect on both hot and cold working.

For special purposes iron, manganese, chromium, silicon, and aluminum are frequently added in varying amounts, but cause no cracking difficulties in rolling or extrusion.

The major quantity of commercial ternary copper-nickel-zinc alloys contain from 10 to 20 per cent nickel (a few up to 30 per cent) and range from 44 to 70 per cent copper, with zinc and minor additions such as manganese the remainder. Single-phase alloys are known as nickel silvers, while those of the beta and alpha-plus-beta phase structure may be referred to as either nickel silver or nickel brass.

The alpha alloys containing 58 per cent copper or more are less ductile and more critical in the effect of temperature than the alpha brasses. Consequently, they are usually preheated to a higher temperature—900°C (1650°F). They are also adversely affected by small quantities of lead and other impurities discussed with reference to cupro-nickel and, as with alpha brass, the maximum lead is usually limited to 0.02 per cent or less because most of these alloys are hot rolled to sheet or strip.

The beta and alpha-plus-beta alloys containing 6 to 18 per cent nickel and 38 to 45 per cent zinc, like the corresponding copper-zinc alloy, can be hot worked in extrusion and forging over a wide range of temperature.

The alloy containing 45 per cent each of copper and zinc has very good hot-working properties, but with increasing nickel content the alloy becomes less readily extrudable.

It is known that phosphorus adversely affects the hot working of these alloys, but no definite limits are set because all metal that may contain phosphorus, such as scrap phosphorus-deoxidized copper, is avoided in the melting.

Lead does not affect the extrudability but seriously impairs the forging behavior.

Other elements such as manganese, silicon, and iron within the limits present through commercial practice have no adverse effect on either extrusion or forging.

Tin Bronze; Phosphor Bronze

Most commercial copper-tin alloys and practically all those fabricated by working contain phosphorus in the range of 0.02 to 0.35 per cent and for this reason are usually referred to as phosphor bronze.

Tin, if added to copper containing cuprous oxide, will deoxidize the copper but form tin oxide that remains as inclusions in the castings. Therefore, a sufficient quantity of phosphorus is added before the tin addition to deoxidize the copper and leave a minimum of 0.015 per cent phosphorus in excess. However, a larger excess is frequently used to obtain the higher tensile strength and hardness needed for the end use.

The major portion of the alloys intended for hot working range from 1.5 to 11 per cent tin. However, it is reported that alloys up to 16 per cent tin are commercially hot worked[22].

The alpha phase, which is the principal constituent of commercial alloys, is weak at elevated temperature and in addition a low-melting metastable copper-tin-phosphorus complex may be present. These alloys are also adversely affected by very small amounts of lead, bismuth, antimony, and other impurities. The result of these factors is that the phosphor bronzes are considered to be the most difficult of the copper-base alloys to hot work.

The lower-tin alloys ranging from 1.5 to approximately 7 or 8 per cent can be more easily hot worked than the higher-tin alloys, but all require careful and prolonged heating within a narrow temperature range for successful results.

Phosphor bronze can be hot rolled, forged, or extruded provided the special care indicated is practiced, but high roll and extrusion pressures are required and consequently relatively heavy equipment is needed.

In extrusion phosphor bronze behaves quite differently from brass or most other copper alloys, and in addition to higher pressures it requires a coordination of temperature and extrusion speed control with composition and shape to avoid "fire cracking" or disintegration of the product. Too high a temperature or extrusion speed is particularly detrimental. The maximum hot-working temperature is determined by the tin and phosphorus contents, the lower percentages allowing higher maximum temperatures.

A satisfactory rolling temperature for 1.25 per cent tin, approximately 0.1 per cent phosphorus alloy is 800 to 850°C (1470 to 1560°F), and for 7 per cent tin, 0.1 per cent phosphorus a temperature several hundred degrees lower would be most satisfactory.

Because of the high extrusion pressure required it is advantageous to operate as near the maximum permissible for the alloy and shape as possible. As the difficulties increase with increasing tin and phosphorus, the process is limited at present to those alloys under approximately 8 per cent tin and 0.25 per cent phosphorus.

The lower-tin bronzes up to about 5 per cent tin and under 0.1 per cent *phosphorus can be extruded with controlled speed at about 800 to 850°C* (1470 to 1560°F).

In commercial practice the maximum limits allowed for lead and bismuth are usually set at those established for deoxidized high-purity copper, and in addition only the highest-purity tin is used in order to limit elements such as antimony, arsenic, etc., to very low concentrations.

Silicon Bronze

The silicon bronzes are single-phase alloys containing from 1.5 to 3.25 per cent silicon and from 0.15 to 1.25 per cent manganese and can be hot worked by rolling, extruding, and forging. Small additions of tin and zinc are sometimes made for special purposes without adverse effect on hot-working properties.

These alloys have relatively high strength at elevated temperatures and are therefore hot worked at temperatures as near as possible to the upper limit of the ductile range. The preheat temperatures range from approximately 850 to 900°C (1560 to 1650°F).

They are also made hot short by small quantities of impurities, in the same order of magnitude, as the alpha alloys of zinc and nickel, and it is usual in commercial practice to apply the same maximum limits. The maximum lead allowed is usually 0.02 per cent or less, although much more can be tolerated in metal to be extruded.

Aluminum Bronzes

Aluminum forms a series of alloys with copper that are similar in hot-working characteristics to the corresponding brass series.

The beta alloys containing from 9 to 11 per cent aluminum plus various amounts and combinations of nickel, manganese, and iron have very good hot-working properties like the beta brasses, and can be rolled, extruded, and forged over a wide temperature range, as they have no brittle range up to 950°C (1745°F).

The alpha and alpha-plus-beta series, like the corresponding brass series, can be hot rolled or extruded if relatively free from lead and bismuth. Nickel, manganese, and iron are also added to these alloys with no adverse effect on the hot-working characteristics.

Lead is added to these alloys for the production of free-machining forgings; however, the forging stock must be extruded, as this element in the quantity needed for this purpose will cause severe cracking in rolling.

HOT-WORKING OPERATIONS

Hot Rolling

The major tonnage of flat rolled products is hot rolled from cake weighing from 600 to 2,000 pounds on the initial heat, a smaller tonnage being rolled from cake up to 10,000 pounds. Rolling practice is quite similar for all the modern mills. Examples illustrating the procedure are:

Copper: cast cake 4 by 24 by 33 inches long, weight 1,000 pounds, reduced to approximately 0.38 inch in 11 passes through the rolls.

70-30 brass: cast slabs, 4½ inches thick by 25 inches wide by 59 inches long, weight approximately 2,000 pounds, reduced to approximately 0.38 inch in 13 passes.

A popular size mill has 26-inch diameter chilled iron or forged steel rolls 46 inches wide. A few two-high reversing mills with rolls approximately 10 feet wide are used for rolling exceptionally large and heavy plate weighing up to 10,000 pounds or more.

The two-high reversing mill is preferred for hot breakdown rolling operations because slabs of more uniform gage can be produced at a faster rate, and when equipped with edging rolls can produce slabs at more uniform width having better edges and consequently less scrap from edge trimming. Figure 28-3 shows a modern two-high reversing mill equipped with edging rolls. Water cooling is necessary to prevent the rolls from overheating and to maintain the roll contour. Provision is also made to apply either oil or an oil-water emulsion to the rolls as the metal passes through them in order to prevent oxide scale lifting from the metal surface and adhering to the rolls.

Most mills are driven by suitable speed-reducing gears from approximately 1,000-horsepower motors, the peripheral speed of the rolls being around 200 to 250 feet per minute. Because of the hot and heavy material being handled, the mills are fully mechanized with mechanical conveyors and other handling devices, particular attention being given to the design and operation to assure that no gouging or scratching of the hot metal occurs in the process.

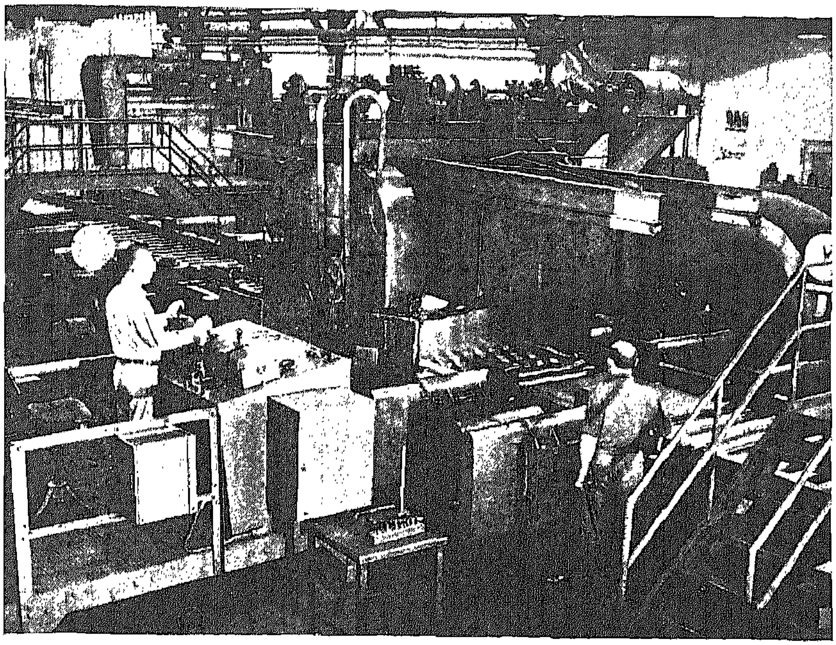


FIGURE 28-3. Two-high reversing mill. (*Courtesy of Revere Copper and Brass Incorporated.*)

Sheet and strip copper and copper alloys are produced in a large number of widths and in relatively small lots as compared with steel. Consequently, economics require that this condition be met by rolling from a limited number of cake sizes. Therefore, it is often necessary to corner or turn (cross roll) the slabs in the initial passes to obtain the required width.

After the last pass the slabs are conveyed to a suitable acid pickling bath, washed and brushed and roll-leveled in one continuous operation. The resulting slabs are then conveyed to the cold-rolling mills for special products.

Hot pack rolling, *i.e.*, the rolling together of two or more slabs approximately 0.38 inch thick to produce thin sheets, has been practically abandoned in the United States, but is practiced to a limited extent in Europe.

The tensile strength and elongation of hot-rolled copper and some copper alloys are given in Table 28-2.

Rod Rolling

While there is a difference of opinion regarding the merits of the two-high continuous mill such as used for rolling steel rod and the three-high Belgium looping mill, the latter is in more general use for rolling copper and copper alloys.

The advantage of the high production rate and possibly lower cost of the two-high tandem mill is claimed to be overcome by the flexibility and quality of the finished products produced by the Belgium mill.

Both types of mills use grooved rolls of chilled or alloyed iron. The grooves are designed to make a series of reductions starting from the standard dimensions of the various size wirebars as listed in the standard specifications of the *American Society for Testing Materials for electrolytic copper*. A typical series of grooves for the production of approximately $\frac{5}{16}$-inch diameter copper rods from a 250-pound (approximately $4\frac{1}{4}$ by 4 by 54 inches) wirebar is shown in Figure 28-4. The number of grooves (passes) used for producing $\frac{1}{2}$-inch diameter or $\frac{5}{16}$-inch diameter rod will vary from approximately 14 to 18. The Belgium-type mill is generally arranged with a breakdown roll having three or more reductions located ahead of the intermediate and finishing train of rolls, which are in a straight line with motors located at each end of the train.

In the breakdown roll the bars pass completely through one groove before entering the next groove in a reversed direction. In the intermediate and finishing train the metal has become sufficiently elongated and flexible that it can be looped from one groove to the next in a continuous "snake-like" fashion, the reductions and speed being so proportioned that an excess of metal is delivered from one groove over that needed for the succeeding groove. Consequently this excess forms a loop between the grooves and from this the name "looping mill" is derived.

The first-pass groove in rod mills is either gothic (Figure 28-4-1), box (Figure 28-4-2), or diamond (Figure 28-4-4), which is a square with one diagonal parallel to the roll face and the other diagonal at 90° to the roll face (Figure 28-4-3), arranged so that the penultimate groove is oval, as this shape is more suitable than the square for conversion to a round in the last groove.

Most mills are designed to roll a finished rod approximately $\frac{1}{4}$ to $\frac{3}{4}$ inch in diameter, $\frac{5}{16}$-inch diameter being the most popular size.

All mills are equipped with suitable guides placed in front of each groove, the oval sections being entered into the square grooves in an upright position in order to obtain maximum reduction in area with a minimum of lateral flow, and the square sections are entered into the oval grooves with the diagonal at 90° to the face of the rolls for the same reason.

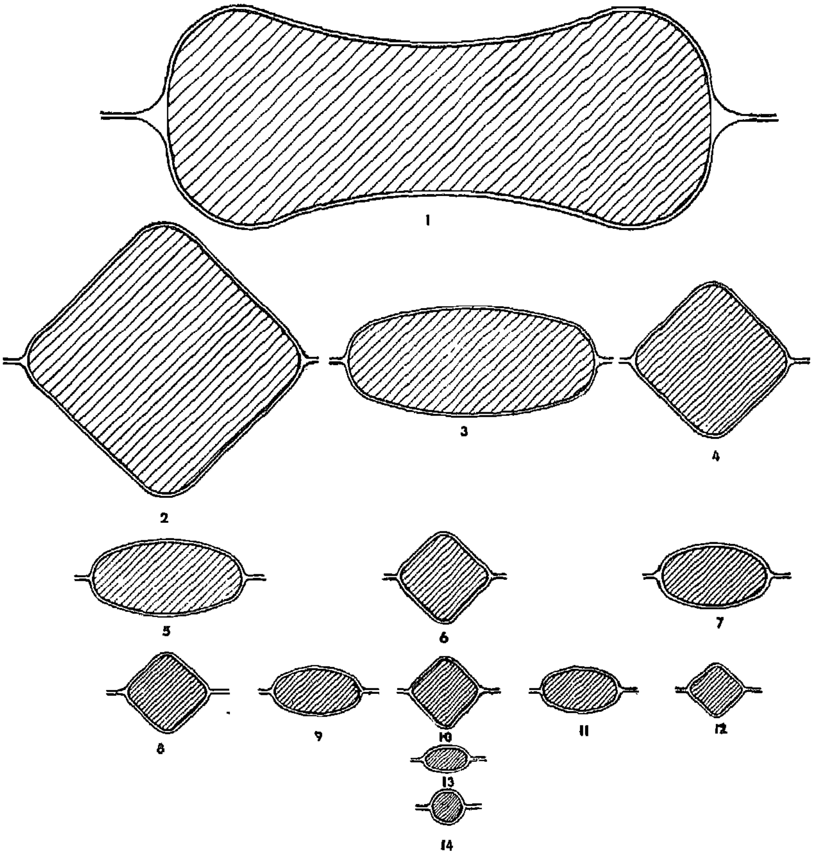


FIGURE 28-4. Diagrammatic representation of typical contours of passes suitable for rolling bars and rod.

It is an important element of design that the reductions in area for each groove be proportioned to prevent the lateral flow of the metal from overfilling and consequently forming fins between the rolls, and it is for this reason that the size of the grooves is changed for rolling certain alloys, particularly Muntz metal, naval brass, and oxygen-free copper, as these spread more than electrolytic copper.

Water jets are used to cool the rolls and these are directed at the grooves and are of sufficient velocity to dislodge any loose particles of scale from the rods or roll grooves.

As indicated above, the Belgium mills are set up in three sections, *i.e.*, breakdown rolls, intermediate rolls, and finishing rolls, each section being run at a higher speed than the preceding section. The finishing speed varies from approximately 1,000 to 1,500 feet per minute or more depending upon the size of the mill and the diameter of the rod being rolled.

The rod is delivered from the last groove to horizontal coilers and then conveyed to acid pickling and washing tubs where the oxide is removed by solution in sulfuric acid and the fine copper remaining from the decomposition of the cuprous oxide is washed off by high-pressure water sprays.

In most mills the copper is recovered from the pickling solution by a small electrolytic copper plant using insoluble lead anodes, the amount of copper recovered being approximately 0.2 per cent of the weight of the copper rolled.

Figure 28-5[23], showing the per cent reduction per pass and mill data for rolling copper rod, illustrates the variations in commercial practice and presents a good résumé of the mechanical and operating data on three important mills in the United States.

While there are significant differences in the design of various mills and in the operating practice, it is generally agreed that the first heavy reducing grooves of the breakdown mill should be designed in relation to the dimensions of the entering bar so that the bar is supported on all sides and corners to avoid cracking and to prevent overfills (*i.e.*, the metal flowing into the small space between the upper and lower rolls) which produce fins or slivers in the finished products as they are rolled over in subsequent passes.

Oversize bars are rejected, as these increase the normal amount of reduction and cause overfills.

The surface of the first groove is sometimes roughened to facilitate entry of the bar, but excessive roughening or gouging is generally avoided as such practice results in tearing the surface of the metal and lowering both the physical and surface quality of the rods produced.

Special Shapes

Merchant mills similar in layout to those used for rolling iron are used for special copper shapes such as commutator bars, small bus bars, irregular sections, and also for copper alloys. These are usually smaller and slower mills and are more flexible in that they are designed to handle a large variety of sizes of copper and alloys in relatively small lots with minimum time lost in roll changes.

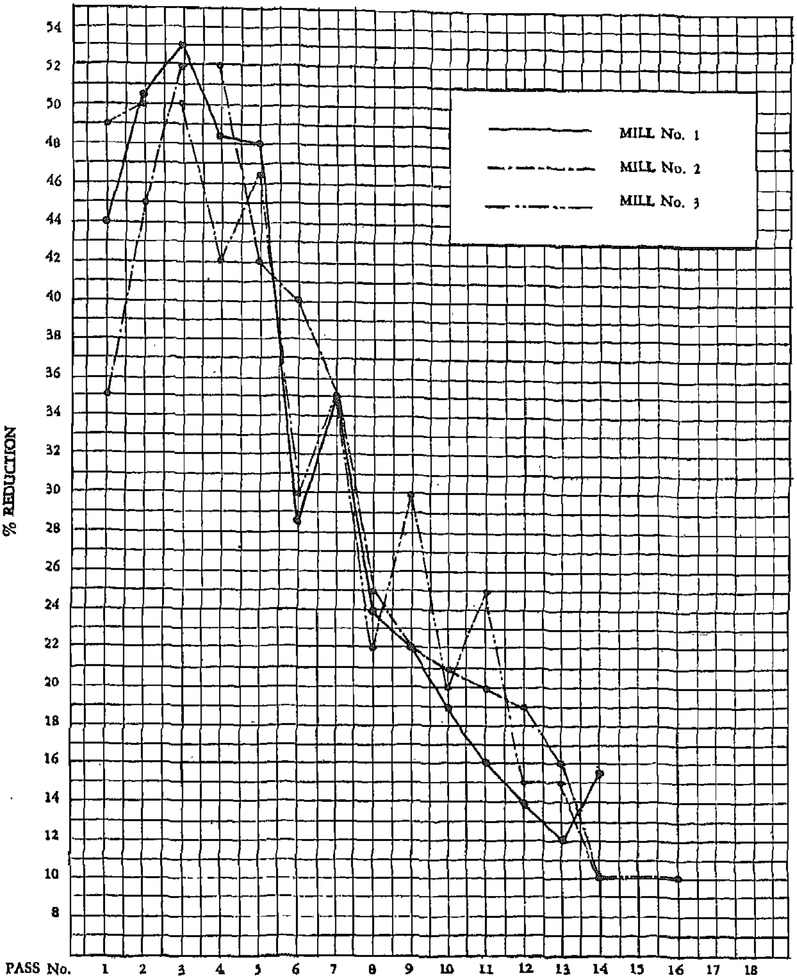


FIGURE 28-5. Graph showing percentage reduction in copper rod rolling mills.

The products rolled are usually larger in cross section than those rolled on wire mills, and many are not suitable for looping from one groove to another. Therefore, these heavier sections are run completely through one groove before entering the other. Consequently there is less mechanical handling.

All metallurgical factors, such as heating to rolling temperature without the formation of excessive scale, or hydrogen embrittlement, correct design of initial grooves to avoid cracking, etc., are the same and controlled as described for rolling in looping mills.

Rotary Piercing

Practically all copper tubing is of the seamless type produced by piercing a solid billet to form a hollow shell suitable for drawing on standard drawbenches. These machines vary somewhat in design but all embody the same basic principles of the original Mannesmann piercer.

Figure 28-6, taken from the Mannesmann patent granted in 1886, illustrates the fundamental principles incorporated in these machines and shows the two-roll type. However, some machines are equipped with three barrel-shape driven rolls instead of two, and in another type bevelled disks are used in place of rolls.

Referring to Figure 28-6, the driving rolls are coupled through long spindles to a motor-driven common reduction gear so that both rolls rotate at the same speed and direction. The horizontal axes of the rolls are at an angle to one another. The angle formed at the intersection of these axes is known as the angle of inclination. This angular setting of the rolls provides the helical rotary motion that advances the billet in

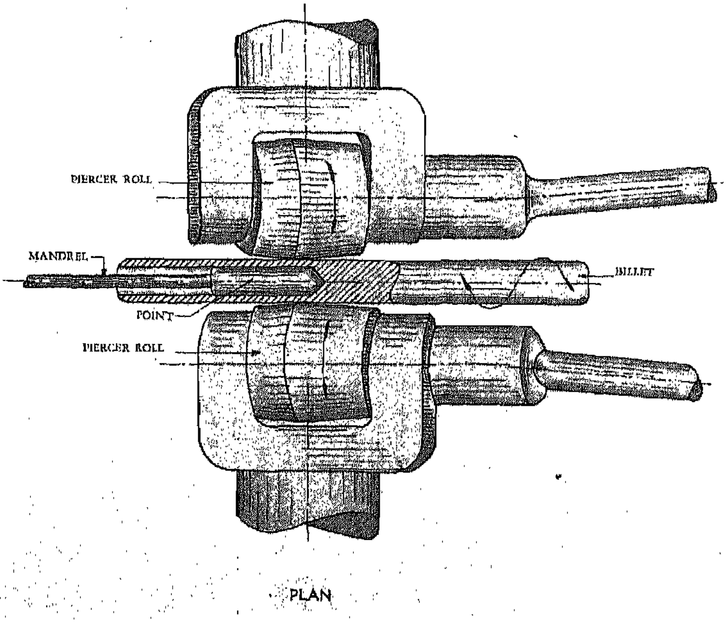
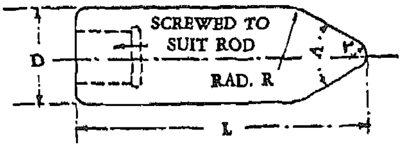


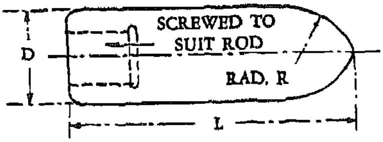
Figure 28-6. Typical piercer mill.

a direction toward the piercing point on the mandrel. Parallel rolls would rotate but not push the billet.

The angle of inclination is fixed in some machines and adjustable in others, and determines the rate at which the billet advances. Although this angle is not very critical, it has definite limits; too small an angle



DIAM. OF BILLET	D	L	R	A	r	USED FOR
3"	2¼"	11"	1"	60°	¼"	COPPER
3	2⅝	11	1	60	¼	COPPER
4	2¾	11	1	60	¼	COPPER
4	3	11	1	60	¼	BRASS 85/15 AND 90/10
4	3⅜	11	1	60	¼	COPPER
4⅛	3½	11	1	60	¼	BRASS 85/15
8	6⅞	11	5	60	½	COPPER
8	6⅞	11	5	60	½	BRASS 85/15



DIAM. OF BILLET	D	L	R	USED FOR
3"	2⅜"	11"	2⅜"	BRASS 70/30
8	6⅞	11	6⅞	BRASS 70/30

FIGURE 28-7. Types and sizes of points, rotary piercer.

slows up the output and if carried to extreme the trailing end of the billet will not open to pass over the piercing point. Conversely, increasing the angle increases the speed until excessive slippage ruptures the metal and drags laps over the surface. It is general practice to use an angle of approximately 6° for piercing copper and copper alloys.

The rolls on the inlet side of the machine are usually tapered about 5° and the outlet side from 3 to 10°. The inlet angle is one of the factors determining the forward driving force on the billet and the outlet angle one of the factors that determines the outside diameter of the tube shell produced. An angle of approximately 8° produces a tube shell having about the same diameter as the billet from which it was pierced. Smaller angles produce a shell diameter smaller than the billet diameter.

Large-diameter copper tubes are sometimes produced in two separate piercing operations. In the first operation, billets 8 or 9 inches in diameter are pierced to produce tube shells of the same diameter, and then put through the machine again to produce 10 to 12-inch diameters.

The distance between the maximum roll diameters is adjustable and is usually set to approximately 0.8 of the billet diameter. This adjustment is varied by trial and error to obtain optimum results for the particular metal being pierced.

Practically all copper and copper alloys are pierced from cast billets

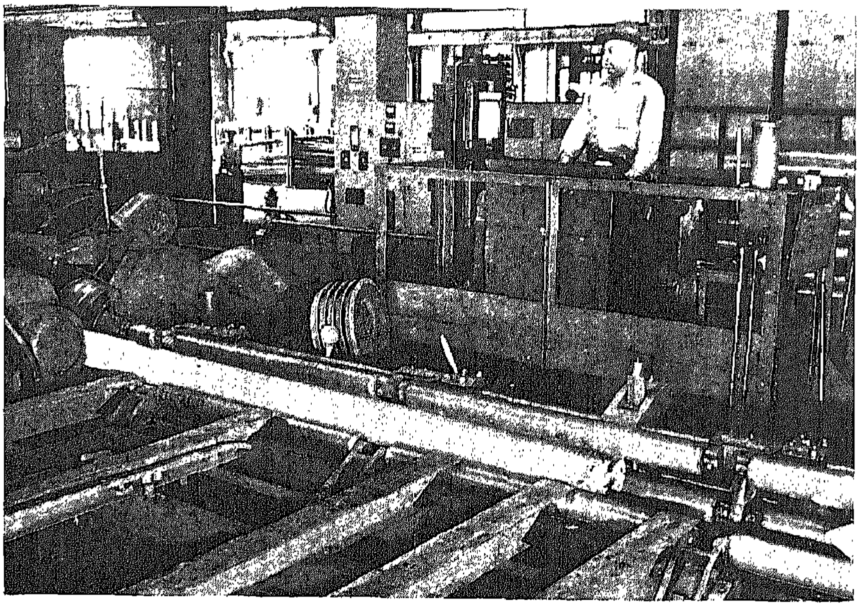


FIGURE 28-8. Tube piercer. (*Courtesy of Revere Copper and Brass Incorporated.*)

and consequently have a cast crystal structure. In the piercing operation the crystals separate because of the torsional force immediately in front of the piercing point, the point and other adjustments being made to accomplish this so that the point serves as a rolling surface to reshape the metal as it passes through the outlet side of the rolls.

The metal is forced over the point to obtain a smooth round tube, as a rough and irregular tube can be produced on these machines without the use of a point. The design of pierced points used in the various mills may vary considerably, as each operator has developed his own design from experiment and experience; the drawings and tabulation shown in Figure 28-7 illustrate those used in commercial practice for copper and some copper alloys.

All grades of commercial copper, the alpha copper-zinc alloys, provided the lead content is held to less than approximately 0.01 per cent, the alpha-beta zinc alloys with lead up to 1 per cent, naval brass, and leaded naval brass are all readily pierced.

The piercing operation requires close temperature control because the permissible temperature ranges for piercing alloys are small, and it is general practice to use radiation-type instruments that sight directly on the billets to indicate their temperature. If the temperature is too high, cracks may form on the inside surface, causing rejection, while cold billets would slow up the operation or stick in the machine. The temperatures generally used for alloys commonly processed by piercing are listed in Table 28-3.

Most alloys are pierced from billets ranging between 3 and 9 inches in diameter by approximately 4 feet long. Copper and copper-zinc alloy billets of these sizes can all be pierced in about 15 seconds. However, the surface speed of the rolls is adjusted to a slower speed for the higher-zinc alloys.

TABLE 28-3. COPPER ALLOYS COMMONLY PIERCED (TUBE)[2]

			Mechanical Properties as Pierced[b]	
Metal[a]	Copper, Per Cent	Initial Temperature for Piercing, deg. Fahr.	Tensile Strength, psi	Percentage Elongation in 2 inches
Electrolytic copper	99.92	1500 to 1600	33,000	35
Deoxidized copper	99.95	1500 to 1600	33,000	35
Commercial bronze	90	1500 to 1600	35,000	40
Red brass	85	1500 to 1600	40,000	40
Cartridge brass	70	1400 to 1450	45,000	45
Muntz metal	60	1300 to 1400	50,000	45
Naval brass	60	1350 to 1450	52,000	45

[a] See Table 28-1 for nominal compositions of these metals.
[b] The mechanical properties shown are average and are not to be used as minimum requirements.

The maximum power required varies from approximately 1,000 to 1,400 horsepower, the alloys generally requiring the higher power.

After piercing, the shells are quenched in water and pickled, before delivery to the drawbenches.

Extrusion

The process of extrusion consists in heating metal, in the form of cast billets, to a plastic temperature range, placing this heated billet into the cylinder of a high-pressure hydraulic press, and forcing the plastic metal through one or more shaped orifices or dies. The old tube-extrusion process wherein a cast hollow billet was extruded over a mandrel is almost obsolete, having been replaced by the modern method of extruding from solid billets.

The use of extrusion for the production of tubes, rods, and other shapes has been increasing rapidly and at present a large tonnage of a wide range of copper and copper alloys is in commercial production. Some of the most commonly processed alloys, their tensile strength and elongation, also their initial extrusion temperature, are listed in Table 28-4.

Some of the reasons for the increasing use of extrusion are that surface quality of the products is generally superior to those produced by rolling or piercing, more complicated shapes can be produced, and alloys too hot short to be rolled or pierced can be successfully extruded.

Most condenser and other tubes requiring a surface of superior quality are drawn from extruded tube shells. Architectural and other bronze shapes, as well as forging rod, are made almost exclusively by extrusion.

Extrusion billets vary in size from approximately 4⅝ inches in diameter by 7 inches long for small vertical presses to 10 inches in diameter by 30 inches long (weighing 800 pounds) for large horizontal presses.

There are several types of billet-heating furnaces in use, but all are of sufficient capacity to bring the metal to a uniform temperature, and in most mills the temperature of each billet is checked with a radiation pyrometer before being placed in the extrusion press.

Old-type vertical presses of 600 to 1,100 tons capacity are rapidly being replaced with large horizontal presses having a capacity of 2,500 to 7,500 tons. Vertical presses are used exclusively for tube shells, as concentric tubes are more easily produced. However, with proper maintenance and use of center-drilled billets, horizontal presses produce tube shells within permitted commercial tolerance of 15 per cent plus or minus the wall thickness, most being within 10 per cent.

TABLE 28-4. COPPER ALLOYS COMMONLY PROCESSED BY EXTRUSION (ROD, BAR, AND TUBE)[2]

Metal[a]	Copper, Per Cent	Initial Temperature for Extrusion, deg. Fahr.	Mechanical Properties as Extruded[b]			
			Rod and Bar		Tube	
			Tensile Strength, psi	Percentage Elongation in 2 inches	Tensile Strength, psi	Percentage Elongation in 2 inches
Electrolytic copper	99.92	1500 to 1650	32,000	40	......	....
Deoxidized copper	99.95	1500 to 1650	32,000	40	......	....
Leaded copper	99.0	1500 to 1650	32,000	40	......	....
Red brass	85.0	1450 to 1600	......	....	38,000	50
Muntz metal	60.0	1250 to 1350	52,000	45	......	....
Free-cutting brass	61.5	1300 to 1400	48,000	45	......	....
Forging brass	60.0	1250 to 1350	50.000	45	......	....
Architectural bronze	57.0	1200 to 1300	54,000	45	......	....
Admiralty metal	71.0	1400 to 1500	......	....	46,000	65
Naval brass	60.0	1200 to 1350	55,000	45	......	....
Leaded naval brass	60.0	1200 to 1350	55.000	45	......	....
Aluminum brass	76.0	1450 to 1550	......	....	48,000	65
Aluminum bronze, 5%	95.0	1500 to 1600	50,000	60	50,000	55
Aluminum bronze, 8%	92.0	1350 to 1450	60.000	60	......	....
Cupro-nickel, 30%	70.0	1900 to 2000	......	....	54,000	35
Cupro-nickel, 20%	80.0	1800 to 1900	......	....	48,000	40
High-silicon bronze (A)	96.0	1400 to 1500	53.000	70	53,000	65

[a] See Table 28-1 for nominal compositions of these metals.
[b] *The mechanical properties shown are average and are not to be used as minimum requirements.*

There are two methods of extrusion, one known as the direct method and the other the indirect or inverted method.

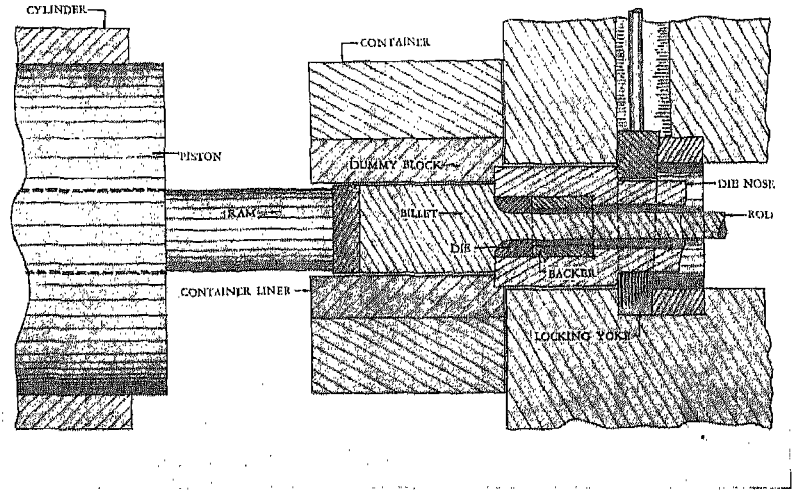


Figure 28-9a. Rod extrusion press.

In the direct method the pressure for extrusion is applied through the ram to one end of the billet, forcing the metal through a die placed at the opposite end, as illustrated in Figure 28-9a. In this method the billet moves forward as extrusion proceeds.

In the indirect method, the die and ram are placed on the same end of the press so that there is no movement of the billet with respect to the container. The metal in this method flows through the die and out of the press through an opening in the ram.

The direct method is much preferred and is in general use for copper and copper alloys, although there has been interest in the different metal-flow characteristics of the indirect method as a possible means of lowering the percentage of scrap by eliminating the defect called pipe or core encountered in direct extrusion, and also because of lower power requirements, as there is no frictional load due to the billet moving along the container wall.

Figure 28-9a, which is self-explanatory, illustrates the extrusion press arrangement for extruding rod or other solid shapes by the direct method and without leaving a sleeve.

Figures 28-9b, c, d, e, and f show diagrammatically the sequence of operations for the more complicated tube extrusion from solid billets, leaving the outer layer of the billet (sleeve) in the container, to be ejected at the end of the cycle and discarded as scrap. In this process the dummy block is about ¼ inch smaller in diameter than the container in order that it may shear through the billet, leaving any defective or oxidized billet surface in the container as a shell or sleeve. This procedure is in most general use because it results in a product of the best quality and produces a minimum of approximately 15 per cent scrap.

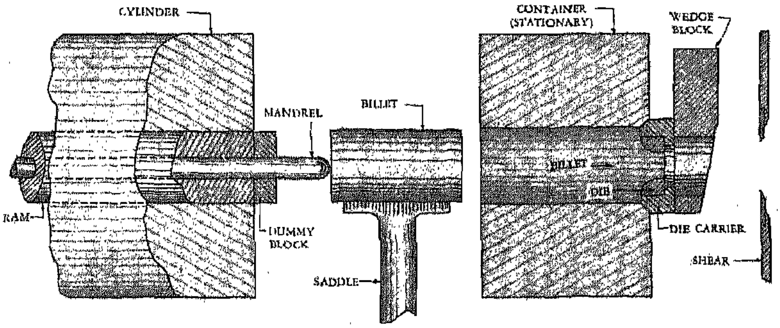


FIGURE 28-9b. Tube extrusion, diagram of operations: Dummy block is placed over end of mandrel and billet is placed on saddle. Forward movement of the mandrel pushes billet into the container. The saddle is then lowered below the path of the cylinder.

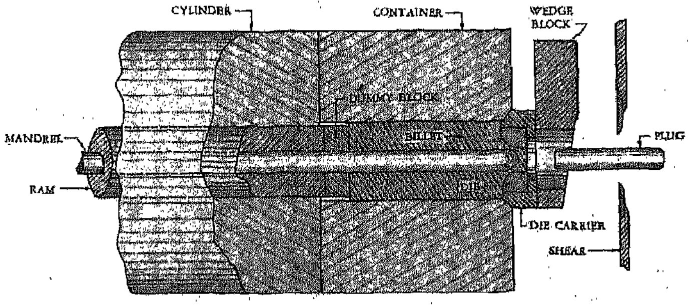


FIGURE 28-9c. Tube extrusion, continued: Ram moves forward and pushes billet against die as the mandrel continues its travel and pushes the plug out of the billet.

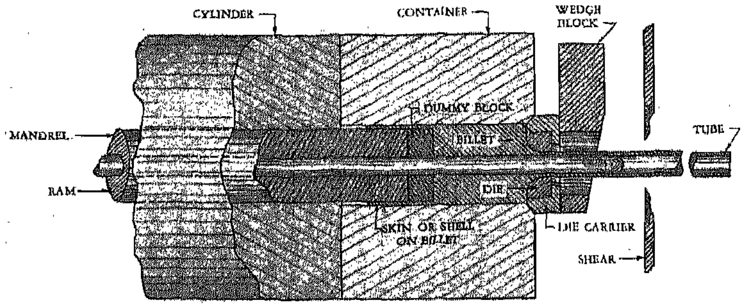


FIGURE 28-9d. Tube extrusion, continued: Mandrel continues forward movement to about 6 inches beyond the die as the ram forces the metal from the billet through *the die and around the mandrel to form the tube.*

In extrusion, the metal flows in a pattern that varies with the design of the die and dummy block, with the copper content, lubrication, and possibly other variables, but numerous experiments have shown that the metal flows first from the center portion of the billet and emerges from the die with a crystal structure quite similar to that of the cast billet.

Friction at the wall of the container retards the flow on the outer portion of the billet, the result being a pattern of flow as illustrated in

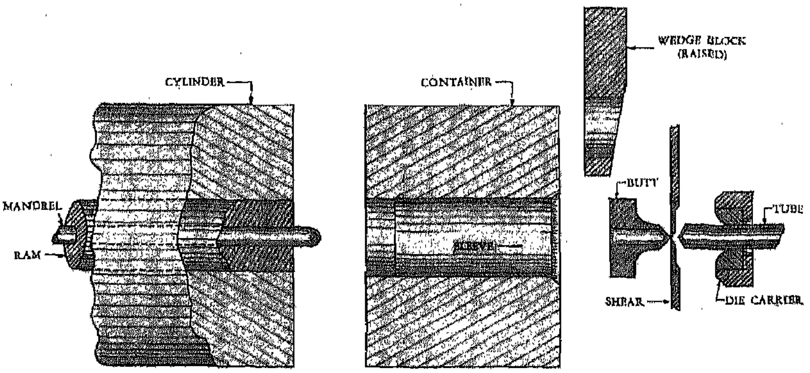


FIGURE 28-9e. Tube extrusion, continued: Forward movement of the ram is stopped momentarily to permit the wedge block to be raised, thus releasing the die and die carrier. The forward movement of the ram continues, forcing the butt end of the tube out of the container for shearing. The dummy block is ejected, the butt is sheared off, and the die and die carrier are removed as the ram and mandrel are retracted.

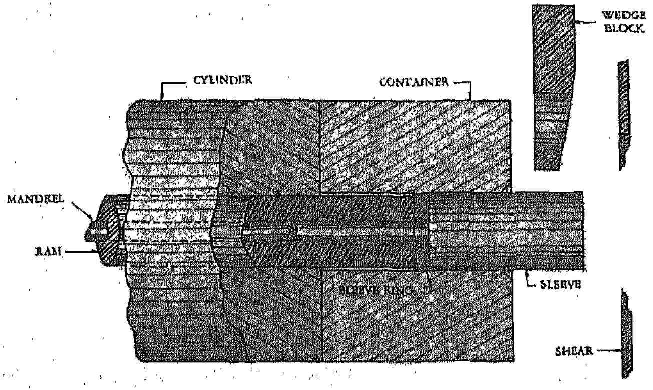


FIGURE 28-9f. Tube extrusion, continued: Retraction of the cylinder permits the insertion of the sleeve ring in the container and forward movement of the ram forces the sleeve out of the container. Cylinder, ram, and mandrel are again retracted and the extruder is then ready for the next billet.

the etched longitudinal sections of brass billets having five copper rods inserted diametrically at regular intervals along the longitudinal axis before extrusion.

Figure 28-9g shows a small distortion of the copper rods from forcing the mandrel, for tube extrusion, through a brass billet. Figure 28-9h shows a similar billet after approximately 40 per cent had been extruded.

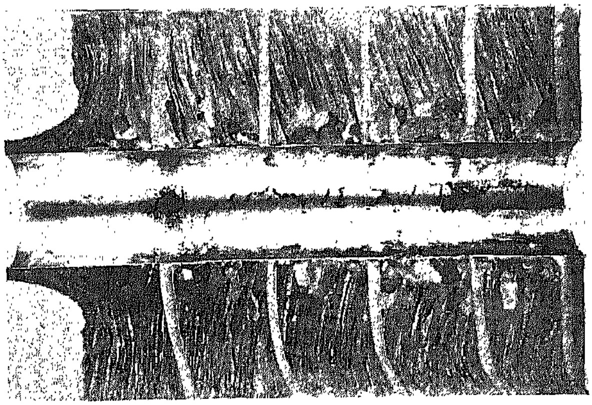


FIGURE 28-9g. Copper rods inserted at intervals along the longitudinal axis of brass billet show only slight distortion from forcing mandrel through the billet.

In this section a portion at the top of the billet has been removed. Part of the copper rod nearest the die has flowed into the tube wall and at the opposite end there is less metal between the copper rod and the end of the billet. Figure 28-9i is a section near the end of extrusion and Figure 28-9j is a section of the discarded billet butt showing portions of all five copper plugs in their final positions.

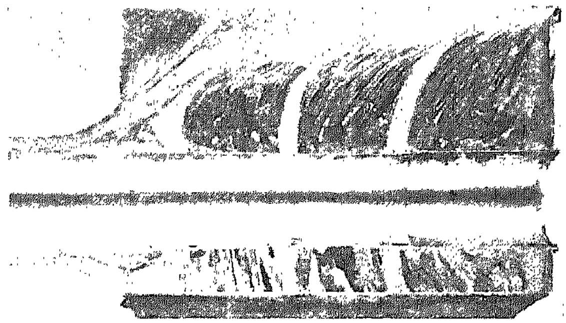


FIGURE 28-9h. Distortion in brass billet after 40 per cent completion of extrusion operation.

As shown in the photographs, the cast crystal structure is gradually refined during the extrusion and results in a corresponding change in the grain size along the length of the extruded tube. The variation in grain size along the length of extrusions is accompanied by corresponding

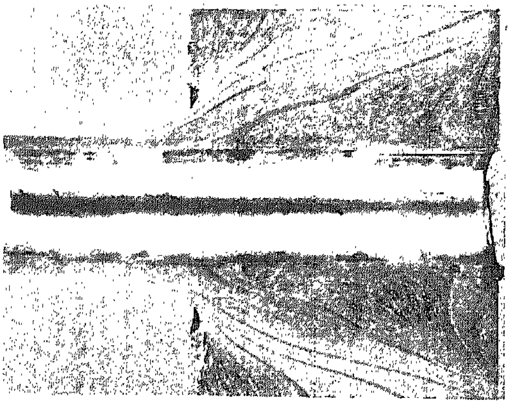


FIGURE 28-9i. Section of billet near the end of extrusion.

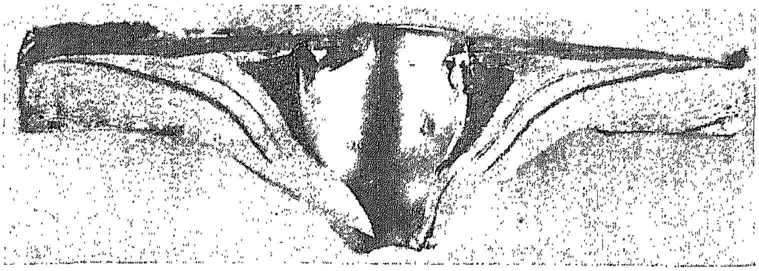


FIGURE 28-9j. Section of discarded butt of billet.

variations in physical properties. Consequently, some alloy extrusions require cold working and annealing to obtain commercial uniformity of physical properties.

The flow pattern illustrated by Figures 28-9g, h, i, and j is that obtained by extruding brass with a sleeve (container not lubricated) in a horizontal press.

Blazey *et al.*,[25] using a similar procedure, investigated the flow in extruding copper and copper alloys with a vertical press and concluded that "the flow is of two types, depending on whether or not the skin of the billet remains in place against the cylinder wall. In a dry or non-lubricated container, brass and copper-nickel alloys flow diagonally to the die orifice, and peripheral portions of the billet are drawn into the body of the billet and carried down between the walls of the extruded tube. In a lubricated container the metal flows from the end of the billet across the die and peripheral portions of the billet are not drawn into the body of the billet to nearly the same extent as with the former type."

In commercial practice all types of copper flow as described for a lubricated container regardless of whether the container is lubricated or not. Blazey *et al.* conclude from their extensive experimentation that this is due to the oxidized surface, always present in commercial operation, that functions as a lubricant for the underlying copper, because they found, under similar extruding conditions, that copper having no oxide coating flows like brass and brass plated with copper flows like solid copper.

The type of flow is of importance, in commercial operations, because it is the most important variable that determines the quantity, location, and type of extrusion defects that may be produced.

Lubrication (such as graphite and oil as used on the die and mandrel) is not applied to the container when extruding in such a way as to leave a sleeve, because it is desired to hold the circumferential layer of the billet in place while the dummy block shears off and extrudes the underlying metal.

Extruding with a sleeve has become the most general practice because surface scale on the billets or minor defects are prevented to a large extent from being extruded into the product.

Some defective material is produced at the finishing end of all commercial extrusions, because it is generally found more economical to extrude the maximum amount of the billet and cut back progressively until all visual surface or internal extrusion defects are eliminated.

In the nonlubricated type of flow, defects at the finishing end are most likely to appear as a core (commonly called extrusion defect) in solid shapes or laminations in tube walls resulting from the oxidized surface of the billet flowing toward the interior at the dummy block and finally into the interior of the extrusion.

In the nonlubricated type of flow, the defects usually appear as blisters or dirty inclusions on the surface or possibly as blistered double-walled tube. Blazey *et al.* found in their experiments that "in the flow obtained with brass in a lubricated container and with copper in either a lubricated or nonlubricated container, defects on the outside of the billet are likely to appear on the outside of an extrusion rather than between the walls." It was also found that with the lubricated type of flow there is a likelihood that the peripheral portion of the billet will fold in across the end near the die and produce a double blistered wall on the extrusion.

The pressure required for extrusion varies with the temperature, extrusion ratio, die shape, metal composition, and other variables and, as to be expected, the temperature and extrusion ratio, *i.e.*, the ratio of billet area to area of extruded shape, have the most influence on the pressure required to extrude any specific alloy.

A number of mathematical equations, proposed by several investigators, for calculating the pressure and power required for extrusion, have been reviewed, correlated and discussed by C. E. Pearson[29]. This review shows that, while considerable information has been obtained on the fundamental aspects of the process, practical success has been attained mainly from empirical knowledge and "cut and try" experiments to ascertain the most satisfactory operating conditions.

The pressure required to extrude copper and copper alloys in commercial practice will vary from approximately 25,000 to 140,000 psi, the higher pressure being needed to extrude silicon bronze and phosphor bronze. The limiting factor is the inability of the steel used for the equipment to withstand the high temperature and pressure involved. Consequently, there is continued interest in the development of alloy steels to withstand these severe conditions.

The pressure cycle starts at a maximum and gradually decreases until near the end of the stroke, when a sudden increase occurs. At this point the extrusion is stopped because it would require an excessive amount of pressure to force the small amount of remaining metal through the die and, as discussed above, this metal would be scrapped because of extrusion defects. The speed of extrusion in commercial practice has a minor effect on the pressure, as economical operations require the highest speed consistent with good quality. The speed is often limited by the shape of the extrusion because of the appearance of closely spaced transverse cracks on the extrusion surface, a condition that is frequently called heat checks because it can usually be corrected by lowering the temperature of the billets, although defective dies or excessive speed may be responsible.

The profile of the dies and the type of alloy or steel used for dies and mandrels vary with local preference, as each mill has based its practice on its own development and experience.

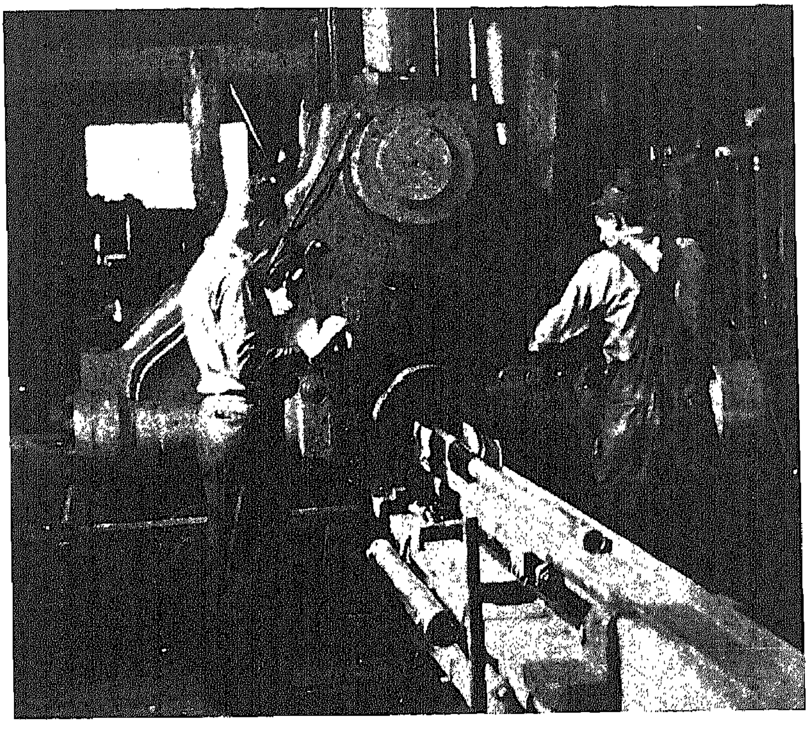


FIGURE 28-10. Tube extrusion press. (*Courtesy of Revere Copper and Brass Incorporated.*)

Features common to extrusion dies for varying purposes are a radius at the die entrance to prevent premature "closing in" (entrance becoming smaller), an angular approach from this entrance to a short bearing (shape and size of desired extrusion), and an angular back relief. These fundamental die features are varied somewhat depending upon the shape of extrusion, metal composition, and, as stated above, the modus operandi developed locally to obtain optimum results.

Alloy steel, stellite, and tungsten carbide have been used for dies with varying success in different mills, and opinion with regard to relative merits is divided.

Forging

Hot forging[26] or pressing is usually defined as the shaping of metal by single or repeated blows under a hammer or press. Many copper alloys, especially those of the alpha-plus-beta and beta types can be forged, the greatest demand being for the brasses and particularly the high-leaded or readily machinable alloys. High-tensile brasses, nickel silvers, and aluminum bronzes are also hot worked by this method. Table 28-5 lists the metals commonly hot forged and pressed as well as usual mechanical properties.

Most of the forgings are relatively small in size and are made from "slugs" cut from previously extruded or chill-cast and scalped stock. Briefly, the process consists in heating the slugs in small preheating furnaces located close by and convenient to the forging hammer or press, then placing these slugs between a set of accurately machined highly polished hardened steel dies of either the open or closed type, and subjecting the metal to one or more blows by a hammer or to a heavy-duty press. The metal flows under compression and fills the contour of the die. Any excess overflowing the die (called "flash") is later trimmed and that present in cavities pierced out. The process is used extensively for the manufacture of ammunition-fuse, refrigeration, automotive, aircraft, plumbing, and other engineering parts. They are usually irregular in shape, having cavities in one plane. However, parts can be made with cavities in two planes by the use of split dies and side rams. These parts usually require machining. The production of forged parts has steadily increased with the growth of the industries enumerated. Forged parts have replaced many formerly produced by machining from heavy castings and consequently are more economical because they require considerably less machining and produce less scrap. Most parts can be forged more economically from slugs cut from round bars. However, some unsymmetrical forgings can best be forged from shapes approximating the shape of the forging.

TABLE 28-5. COPPER ALLOYS COMMONLY HOT FORGED AND PRESSED[3]

Metal[a]	Copper, Per Cent	Suitable Temperature for Forging, deg. Fahr.	Probable Range of Mechanical Properties[b] as Forged				Ability to Be Cut by Cold Shearing
			Tensile Strength, 1000 psi	Yield Strength, 1000 psi	Percentage Elongation in 2 inches	Rockwell Hardness	
Electrolytic copper	99.92	1400 to 1600	30 to 38	8 to 10	45 to 50	F 25 to 65	Yes
Deoxidized copper	99.95	1400 to 1600	30 to 38	8 to 10	45 to 50	F 25 to 65	Yes
Muntz metal	60.0	1150 to 1450	45 to 60	20 to 30	25 to 50	B 35 to 50	Yes
Forging brass	60.0	1200 to 1500	45 to 60	20 to 30	20 to 35	B 35 to 50	Yes
Naval brass	60.0	1200 to 1500	50 to 65	25 to 35	35 to 55	B 45 to 60	Yes
Leaded naval brass	60.0	1200 to 1400	50 to 65	25 to 35	20 to 35	B 45 to 60	Yes
High-silicon bronze (A)	96.0	1300 to 1600	50 to 65	18 to 24	50 to 70	B 35 to 50	Yes
Low-silicon bronze (B)	97.7	1300 to 1600	40 to 55	16 to 22	50 to 70	B 30 to 45	Yes
Aluminum bronze	92.0	1450 to 1600	75 to 90	33 to 40	15 to 30	B 75 to 90	Yes
Aluminum bronze	89.0	1450 to 1550	80 to 90	36 to 45	15 to 30	B 80 to 95	No
Manganese bronze (A)	58.5	1150 to 1450	60 to 75	35 to 45	25 to 45	B 65 to 80	Yes
Manganese bronze (B)	65.5	1150 to 1450	85 to 105	55 to 75	15 to 30	B 85 to 100	No
Nickel silver, 10%, leaded	45.0	1350 to 1500	65 to 75	40 to 50	20 to 40	B 62 to 77	No

[a] See Table 28-1 for nominal compositions of these metals.

[b] The mechanical properties shown are average and are not to be used as minimum requirements.

Forging hammers vary in size from approximately 1,000 to 5,000 pounds, while crank or screw presses vary from 200 to 2,500 tons. Crank and screw presses are used for symmetrical shapes that combine forging and small extrusions in the same operation.

Hammer forging is especially suitable for unsymmetrical shapes or when special shaping and bending are desired. Special forging machines are in use for making small parts or for upsetting operations such as required for bolts.

It is necessary for the dies to be designed with a draft (taper) so that the forgings can be removed. The draft on the dies varies between approximately 1 and 7°, depending upon the design of the forging and the forging machine used. Hammer forgings usually have the larger draft.

Multiple-impression dies are used for economy wherever design and size permit. Suitable allowance for shrinkage upon cooling must be allowed. The number of forgings made from a die depends upon many factors, including the type of steel used and the tolerances permitted. The life of forging dies varies from 5,000 to 100,000 pieces. The dies are lubricated with oil and graphite to facilitate the flow of metal and to prevent metal adherence and overheating of the die.

Forgings can be made to close tolerances, *i.e.*, ±0.005 inch. However, as stated above, close tolerances generally result in considerably reduced die life. Therefore, a tolerance of ±0.010 inch is generally specified.

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Chapter 29

Cold Working of Copper and Copper Alloys

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The plastic deformation of metals can be carried out either in a metallurgically "hot" or "cold" condition, and the capacity of a particular metal to undergo plastic deformation is very important in its position in the metal industry. Cold deformation takes place in the lower range of temperatures below the recrystallization point of the metal involved. In most cases, it is found that the extent of cold deformation has a definite limit, as the metal will become more and more brittle and finally approach the point of failure by cracking. It can then be restored to a condition suitable for further cold working only by an annealing operation.

During cold deformation, the individual grains of the metal become more elongated and increasingly distorted. In the case of heavy deformation, the grains are found difficult to resolve under the microscope because of only slight variation in etching properties. The outer surface of a cold-deformed object will usually be found to finish up smoothly and with some degree of sheen due to actual contact and friction with the forming tools. However, if this surface is allowed to develop freely during cold working, it will be found that each individual crystal deforms in a different manner and a certain degree of roughness will be observed on the metal surface. The degree of roughness will depend on the size of the grain and this roughness is very important on articles to be finished by buffing and polishing.

When estimating the cold-working potentialities of a particular metal, the most important elements to consider are the effects of cold working on the mechanical properties which are related to ductility and strength. The changes that take place in the various mechanical properties during the cold working are closely interrelated. In general, the properties allied with strength and resistance to deformation, such as tensile strength, yield strength, and hardness, increase with increasing degree of cold deformation. Those properties which are allied with ductility, such as elongation and reduction in area, show diminishing values with progressive cold work.

The properties denoting ductility are highest and those denoting strength are lowest in fully annealed material. Elongation values are decidedly reduced by the first small cold deformation and these values then continue to decrease slowly with increasing cold work. Elongation values indicate the extent of cold working that can be accomplished by stretching operations, such as take place in expanding or bulging. Elongation values also serve as a good criterion of the cupping qualities of a material and of the amount of cold working it is capable of taking in a single drawing operation. These values are not, however, a measure of the ability of a metal to undergo successive redrawing operations without annealing.

Reduction-in-area values decrease with progressive cold working but at a slower rate than elongation values. The values of reduction in area serve as good indications of the ability of a metal to take successive redrawing operations without the necessity of reannealing. Material showing high initial reduction in area and comparatively flat reduction-in-area curves, such as is the case with deoxidized copper, is most capable of undergoing repeated cold working or drawing. Tough-pitch copper, which shows lower values of reduction in area than deoxidized copper, is less capable of redrawing operations without reannealing. In the case of yellow brass, the reduction in area drops off much more precipitately than that of copper, showing the need for more frequent process anneals during cold working.

The relative initial annealed values of various copper-base alloys with regard to tensile strength, yield strength, and hardness are of some importance. By them can be judged in a general way the forces that

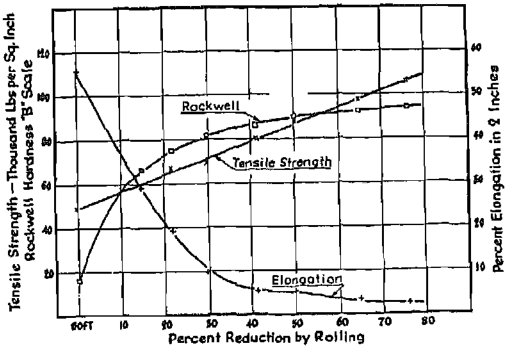

FIGURE 29-1. The effect of cold-rolling on the properties of 70-30 brass.

Material of 0.228-inch gage and 0.125-mm grain size rolled to 0.120-inch gage, annealed to 0.053-mm grain size, and rolled as shown.

will be involved in cold-working operations and some indication of the tool pressures and the size of presses that will be found necessary can be obtained. Also, closely related to the initial annealed properties are the various rates of work hardening shown by the different copper-base alloys.

Rates of work hardening, which are indicated by the slopes of the tensile strength, yield strength, and hardness curves of the particular alloys, are significant in estimating relative deep-drawing properties. With few exceptions, the work-hardening rate varies in proportion to the initial annealed strength of the particular alloy. The highest rates are shown by the stronger, more refractory alloys, such as the aluminum bronzes and silicon bronzes, and the lowest rates of hardening are shown by pure copper. One of the exceptions to this general rule is found in cupro-nickel. Although one of the stronger copper-base alloys, 70-30 cupro-nickel work hardens at a slower rate than yellow brass.

Cold Breakdown; Finish Rolling and Slab-milling of Sheet and Strip

In the discussion of cold working of copper and copper-base alloys, it is well to start with the cold-working processes involved in the manufacture of sheet and strip. Great progress has been made in recent years in both hot and cold rolling; this has been manifested in the increase in weight and width of the rolled bar, in the stepping up of rolling speeds, and in the increase in efficiency of equipment for handling. On many alloys, the original breakdown of the cast bars can be handled both by hot and cold rolling. However, some of these alloys, such as the high-leaded brasses and phosphor bronzes, must of necessity be broken down cold to avoid cracking. Also it is found that for successful hot breakdown of those alloys capable of hot working, impurities such as lead have to be kept to a minimum.

A combination of the above, together with the inherent scrap problem involved and the high percentage of high-leaded mixtures and bronzes characteristic of American mills, makes cold breaking down of ingots for all alloys preferable in many of the largest and most modern mills. In the case of copper strip, the refinery-cast bars are usually broken down hot, the 4-inch thick bars being rolled down to ½ inch before cold-rolling operations are begun.

The modern nonreversing cold-breakdown mill is a two-high mill of 1,000 to 2,000 horsepower containing about 30-inch diameter rolls. This mill is capable of rolling ingots 2½ inches thick, 24 inches wide to about ½-inch gage, *i.e.*, to a point where the bar can be overhauled or slab-milled. As the maximum reduction in this breakdown on copper-base alloys does not exceed 50 to 65 per cent, intervening anneals must be used at various stages to avoid cracking. On mills of the nonreversing type, the slabs are brought to the feed side of the mill in batches, and suitable mechanism is available for returning the bars to this side for consecutive passes. Batch rolling of continuous-cast ingots weighing up to 2,000 pounds is now practical.

Whether the ingots have been broken down hot or cold, when they reach a gage of around 0.400 inch, they usually undergo slab-milling or overhauling on both sides of the bars. There are a few end applications such as roofing copper where the finished surface requirements are such that this overhauling is unnecessary.

This operation is performed on one side at a time in slab-milling installations such as the Torrington machine. These installations contain preliminary multiroll flatteners through which the bars must pass before entering the millers. There are usually two millers laid out in tandem, each containing a high-speed spiral milling cutter. Only the underside of the bar is milled, about 0.010 to 0.020 inch of metal being removed in one operation. Between the two millers, a turnover table permits the unmilled side to be presented to the cutters.

For the rundown and finish rolling of copper and copper-base alloy strip, it is the general practice now to install a small number of powerful high-production mills with efficient handling equipment, each unit designed to deal with one stage of the operation from ingot to finished product. In addition, there are always a number of special-purpose mills, usually small two-high units for use on narrow-width light-gage jobs with close tolerance requirements. Rundown operations, down to about 0.060-inch gage in the case of yellow brass, may be performed in tandem installations consisting of two to five stands of rolls in a series. These roll stands are four-high nonreversing mills, consisting of two 12-inch diameter working rolls and two backing-up rolls approximately 30 inches in diameter. In an installation of this type, the metal is reduced simultaneously in each of the stands and their speeds must be correctly synchronized in order to maintain the correct roll tension.

Various other four-high single-stand mills taking strip up to 25-inch widths and operating at speeds as high as 700 feet per minute have become standard in most brass mills both for rundown and finish operations. These mills are capable of rolling full-width bars down to 0.014-inch gage. The modern type of two-high mill operating at speeds of 250 to 300 feet per minute has still, of course, plenty of applications, especially on the lighter-gage metal with more particular surface requirements.

A recent development that has had some application in copper-alloy rolling is the Sendzimir Multi-rolling mill, involving a cluster of 12 to 20 rolls in one mill. The work rolls on these mills are very small—$\frac{7}{16}$ to $2\frac{3}{8}$ inches in diameter—and they are driven only by the friction of the supporting rolls, which are geared to the driving rolls. The outer support is provided by lines of roller bearings supported by the main frame. As far as the use of this mill on the less refractory metals, such as the copper-base alloys, is concerned, a number of advantages are claimed. These include high rolling speeds and maximum total reductions with accurate gage control at thin gages where the material has already been heavily work hardened.

Miscellaneous Sheet-mill Operations Involving Cold Working

There are a number of other operations in the manufacture of copper-base alloy sheet which may in some degree involve cold working. These include the various types of flattening and leveling operations found in brass mills and such cutting operations as "resquaring and side-shearing," "slitting," etc.

Requirements on cut-to-length strip often include straight edges and ends cut at right angles to the sides. This is known as square-sheared metal. For this operation, large side-shearing presses are used. Thinner-gage strip in lengths over 4 feet, such as the wider copper sheet used for leaders and gutters, may be slit to width and the ends square-sheared in a combination slitter and trimmer known as an "Economy Slitter." Coiled metal may be flattened and cut to length in automatic cutters. The coils first go through flattening rolls, consisting of a number of staggered upper and lower rolls which afford repeated flexing to the strip as it uncoils. The flattened metal is then cut to predetermined lengths by an automatic shear.

For many uses, the finished strip may require special flatness properties. One of two methods of flattening is usually used in brass mills. For coiled stock and material in lengths in heavier gages and harder tempers, roller flattening involving staggered rolls similar to those described above is used. The other method of flattening is known as "Patent Leveling." In this operation, the cut-to-length strip is gripped on both ends in a patent-leveling machine and stretched slightly. Material up to 0.060-inch gage can be handled, but the temper is limited to metal 1 or 2 B & S numbers hard. Little actual hardening or lengthening of the strip takes place in this patent-leveling operation.

Rolled material must have its irregular edges eliminated and must be sheared to correct finish width. Both of these operations are performed in shearing machines or slitters of varying size. In these slitters, a number of disk-shaped cutters are assembled for simultaneous cutting of a corresponding number of strips. The cutters are from 4 to 13 inches in diameter and ⅛ to ¾ inch thick, and are mounted on two parallel shafts rotating in opposite directions. These cutters have two sharp edges and are accurately separated by spacers. There is a distinct tendency during slitting for the cutters to spread, bend, or curl, and power reels are used to rewind the emerging slit metal in order to reduce this distortion.

There are many types and sizes of slitters, each with its individual slitting capacity with regard to minimum and maximum gages. The maximum slitting gage on coil stock is usually limited by the coiler and goes up to about 0.250-inch gage. Flat lengths up to 0.500-inch gage can be slit. The minimum and maximum slitting gages are influenced also by alloy, temper, and the number of cuts.

Cold-working Operations Involved in the Manufacture of Rod and Wire

Copper-base alloy bars, rods, wire, and shapes can be finished to accurate dimensions and varying tempers either by cold drawing or by cold rolling. As a general rule, however, where the alloys permit, the bars are first extruded or hot rolled down to a certain size before the cold-finishing operations.

Many copper-base alloys have to be cold worked all the way down from the castings. These alloys include phosphor bronzes containing over 4 per cent tin, leaded phosphor bronzes, nickel silvers (leaded and nonleaded), and beryllium copper. Cold rolling on round shapes is now used largely as a breakdown operation on alloys of the above types and involves rough rolling followed by a die or rotary scalp. The castings are often square instead of cylindrical and the bars are rolled in alternate diamond or oval grooves and round grooves, with suitable anneals and scalping.

In the nonferrous industry, a recent development has been the multiple-stand cold-rolling installations for breakdown and rundown operations. Ten pairs of grooved rolls are mounted in a straight line and reduce 0.750-inch gage wire to a 0.250-inch gage round-cornered square. The wire is delivered at a maximum speed of 180 feet per minute on a 24-inch coiler at the end of the mill. Total reductions on most copper-base alloys of up to 80 per cent are obtained, although with alloys containing over 1 per cent lead the maximum is around 70 per cent.

The usual method of finishing copper-base alloy rod and wire is by a drawing operation. The extruded, hot-rolled, or cold-rolled stock is given one or more cold-drawing operations to finish, with suitable intermediate anneals. On the rod of larger diameter, which cannot be coiled, this drawing operation is performed on a drawbench.

A drawbench consists of a long frame with a mechanical drive on one end and a die holder and die on the opposite end. An endless square-link chain passes over a sprocket at the driving end of the bench and over an idler at the other end. The sprocket is driven by a motor, and a carriage or pulling head equipped with jaws travels on a track along the top of the drawbench. The carriage is engaged by the continuous chain and pulls the rod through the die. The pointing of the rod previous to drawing is usually performed in swagers using conical or cylindrical dies, although modern drawbenches may be equipped with a pointing head which grips and pushes the rod through the die.

Smaller-size rod is drawn on power-driven blocks or drums. These rotating blocks are equipped with variable-speed motors and the rods are drawn through integrated dies. After finish drawing, the drawn coils are straightened and cut to length in an automatic rotating-head straightener. In rod drawing of this type, various lubricants are used, such as lard oil and tallow. Hardened wrought-steel dies are generally found satisfactory, but sintered carbide dies are sometimes used for the more refractory alloys.

Although a considerable proportion of intricate shapes are made by hot extrusion or hot rolling, some of the simpler shapes requiring more precise dimensions have to be cold drawn to finish. These shapes may be finish drawn not only from rod but also from flat strip or round tube, although the latter will require at least two draws to finish. The alloys finished by cold drawing from extruded rod include architectural bronze, copper, and free-cutting brass; shapes from strip and tubing are made from practically *all* copper-base alloys.

Wire drawing is essentially the same as rod drawing except that the lighter gages in the case of wire permit very long coils to be drawn in one operation. Butt-welding machines are used to permit drawing of continuous wire. The wire is drawn by means of wire-drawn blocks, a single block known as a "bull block" being used for single drafts on heavy-gage wire.

Present-day practice in wire drawing has evolved around the development of the multiple-die machine and continuous-drawing tandem machines. This development has been in conjunction with the development of tungsten carbide drawing dies, which are now employed down to 0.030-inch gage. Below this gage diamond dies are still used.

The multiple-die machines are of the cone type, containing stepped-up cones to compensate for the increasing length of wire. Cone machines may have 12 to 17 dies and in tandem installations they contain 5 to 11 dies. Speeds of the order of 1,500 to 3,500 feet per minute are obtained on tandem machines in drawing heavy-gage stock and up to 5,000 to 8,000 feet per minute on medium fine wire.

The hot-rolled rod, 0.250 inch in diameter, is drawn down to gages ranging from 0.052 to 0.128 inch in 5 to 9-die tandem machines. On this operation, 25 to 30 per cent reductions per draft are involved. If it is necessary to draw the wire finer, the operation is usually performed in a medium light 12 to 21-die machine. The use of a copious supply of lubricant is necessary, especially when drawing copper, and soap solutions of varying fat content are used. It is practical to draw copper about 90 per cent hard before it is necessary to reanneal. Other copper-base alloys, however, can be drawn from 25 to 80 per cent, depending upon the rate of work hardening of the individual metal before annealing is required.

Cold-working Operations Involved in Fabrication of Tubing

The principal method of cold working copper and brass tubing as well as rod and heavy sections not capable of coiling is by means of drawbenches. The tubing originates as heavy extruded or pierced shapes. As in the case of rod and wire, it is possible to take several draws and severe reductions on copper without intermediate anneals due to its low rate of work hardening. The brasses and bronzes, however, require anneals after every draw. The benches used on tubing are similar to those on rod, involving chain-driven pulling heads, die holders, and dies. They are rated by the pounds pull that the main chain and die block will withstand. This capacity varies from 1,000 to 300,000 pounds. The bench lengths vary from 30 to 100 feet and the speeds from 10 to 300 feet per minute.

The most widely used tube bench is the fixed-mandrel type. On this type of bench, there is a mandrel support and a means for adjusting the mandrel relative to the die on the feed end. Also, as is the case on the rod bench, the chain driven in one direction moves the carriage along the structural section. After completion of the draw, the carriage is returned by a cable. Previous to drawing, the tube must undergo mechanical pointing by hammering or squeezing between die blocks to the correct diameter. The actual drawing of the tube is performed by one of three methods, and in the process of drawing the outside diameter, the inside diameter, and usually the tube walls are reduced.

The first of these methods of drawing makes use of a fixed mandrel or plug and there is a simultaneous reduction in outside diameter and wall. The mandrel or plug consists of a short cylindrical or tapered steel rod attached to a long rod of smaller cross section, rigidly held by a bracket at the end of the drawbench. Floating plugs of a stepped contour which automatically adjust themselves to the correct position during drawing have recently been used.

The process of drawing involves threading the tube over the hollow mandrel, passing the tube point through the carbide or chrome-plated steel die, gripping the point in the jaws of the carriage, and pulling the tube through. Lubricant is applied either by previous dipping in soap solution or piping solution through the hollow mandrel.

The second method of bench drawing involves the use of a movable arbor. The tube is threaded over an arbor tapered 0.06 to 0.10 inch to facilitate extraction, and both the arbor and tube are drawn through the die together. It is not necessary to point the tube, and the inside diameter of the tube is controlled by the arbor size. After each reduction, it is necessary to free the rod from the tube by a roller straightener (Medarting) or swaging operation. This type of drawing is generally restricted to small tubing where a plug rod would be too weak, or else to thin-wall tubing where the plug might damage the tube.

Hydraulic and mechanical push bench equipment with a rod-type mandrel similar to that described above is used for drawing heavy-gage tubing. On the reverse stroke, the tube is stripped from the arbor against mechanical strippers.

In the third type of tube drawing, known as "sinking," no mandrel or interior tool is used and the tube is simply pulled through a die. Both the outside diameter and inside diameter of the tube are reduced, but the wall gage usually thickens as much as 5 per cent. In sink draws, the inside surface does not finish as shiny and smoothly polished as is the case in plug and arbor draws.

Sunk tubes are apt to finish with very high internal or residual stresses. The presence of such stresses in the case of brass and other copper-base alloys may result in a tendency to season cracking. However, it is found that if the decrease in diameter amounts to less than about 50 per cent reduction in area, there is little danger of season cracking even in the case of sensitive yellow brass.

In addition to drawing, the diameter and wall of tubing may also be reduced by "tube rocking." "Rocking" involves severe reductions up to 75 per cent, but it is a slow, expensive method of tube reduction. The main advantage of this method of cold reduction is that it tends to eliminate eccentricity better than drawing and the more refractory alloys, such as the aluminum bronzes and brasses and cupro-nickels, are reduced in this manner.

The operation of tube rocking involves the cold sizing of a tube by means of semicircular grooved dies that are rocked back and forth over the tube. This rocking takes place over a mandrel that controls the inside diameter of the tube. The grooves of the semicircular die are tapered, one end being somewhat larger than the entering tube. The decreasing area of the grooves and the correspondingly tapered mandrel result in both outside diameter and wall reduction and also in lengthening of the tube.

As the tubes are fed into the rocker, they are continually turned on the tube axis so that the cold work is distributed around the circumference. The result of this simultaneous turning and rocking is a tube with accurately controlled dimensions. During the operation, the forward motion of the tube is about 17 inches per minute, resulting in a reduction, for example, from 2½ inches extruded size to $1\frac{9}{16}$ inches. If two rocks are involved, the tube may be brought down to 1⅛-inch diameter by a die change. Soap lubricant constantly pours on the work and there is an integrated saw in the installation.

Press Operations Involving Blanking, Punching, and Perforating

In a blanking operation, flat pieces of the desired shape are cut from sheet in a press using sharp-edge punches and blanking dies. The punch diameter is finished between 3 and 10 per cent smaller than the die diameter, depending upon the gage of the metal, and a soft, nonleaded material will require greater clearance than a hard, leaded material. Blanking very thin metal requires sharp tools to avoid burrs and distortion.

The punch used is generally flat faced to prevent bending of the blank, and the pressure requirements are influenced by various factors such as the alloy, gage and temper of the metal, and the clearance, angle, and sharpness of the tools. For example, hard metal requires greater pressure than soft metal and high brass offers greater resistance to the blanking tools than the high-copper low brasses.

The die layout in blanking is such as to allow a distance between two adjacent blanks and the edge of sheet equal to about the thickness of the metal. In order to save material, as efficient a die arrangement as possible is used. For example, a staggered die assembly may increase blank production 20 to 40 per cent. Frequently, double or multiple dies, called "gang" tools, are used, but irregular-shaped blanks are punched with single dies spaced far enough apart so that the strip can be reversed and the blanks taken from the intervening spaces.

The forward progress of the strip being blanked is automatically gaged by one of several means. The gaging action may be performed by a roll feed, a grip feed, or by a finger gage that drops into each blanked hole or possibly into a specially punched hole. The strip is kept in line by guides and the skeleton scrap is removed from the punch by a stripper plate.

"Punching" or "perforating" is a different type of operation from blanking. In the former, the metal actually punched out is the scrap, and the die used is oversize, the punch representing the size of the hole desired. The minimum hole diameter in perforating is equivalent to about the metal thickness and smaller holes should be drilled.

Press Operations of the Squeezing Type

Press operations of this type include coining, embossing, sizing, cold forging, swaging, press forming, and some stampings. All copper-base alloys capable of cold working are capable of these operations, copper being the most easily worked. They are performed in all types of mechanical and hydraulic presses and rope stamps, including knuckle-joint and dual-action presses.

The simplest form of this type of operation, sizing, involves little actual movement of the metal. Examples of sizing operations are the squeezing to proper dimensions and to correct surface of drop forgings and various types of castings and the squaring up of stampings and drawn shells.

Cold forging and swaging operations involve stresses somewhere between the low values required in sizing and the high ones required in embossing and coining. Operations of this type involve formation by the squeezing action of rivet lugs, flange nuts, countergears, and various levers containing bosses and countersinks. Copper is a very popular cold-forging material because of its low rate of work hardening.

Coining and embossing operations involve little metal movement, but may involve considerable build-up of pressure. This is due to the rigidity of press and die construction found necessary, which may build up pressures to several hundred tons per square inch. The object is to bring out sharp accurate lines and designs in a closed die arrangement.

Commercial coining operations are used in making such parts as key blanks and suspender links, and the operations may not only include coining but also subsequent piercing and blanking in a progressive installation. The operations are carried out similarly to actual coin making in heavy presses of knuckle-joint or fully eccentric shaft type.

Embossing involves forming designs on sheet to produce such articles as brass wall plates, box covers, and copper buttons. Designs of varying intricacy are brought out clearly over an extended surface by use of male and female dies. There is little change in metal thickness during embossing and pressure requirements may go up to 1,000 tons per square inch, depending upon the alloy and the success in localizing pressures realized through die design.

Press Operations Involving Cupping and Drawing

Copper, brass, and most copper-base alloys lend themselves well to cupping and drawing operations. Copper has high ductility but also low tenacity and a low rate of work hardening which, in some cases, is found detrimental. It will take severe deformation before reannealing, particularly deformation in one operation. However, unless process anneals are used, breakage will be encountered on certain types of draws requiring high tensile properties in shell walls and involving severe diameter reductions as well as wall reductions. The relatively soft bottoms in copper shells do not withstand well the loads involved in severe reduction of diameter.

For particularly severe drawing jobs, deoxidized or OFHC copper may be used. These oxygen-free types of copper show higher reduction-in-area values than regular tough-pitch copper, and their use may permit elimination of an interstage anneal or draw. With minimum reduction in diameters, deoxidized copper can be drawn almost indefinitely, but requires the use of a sleeve to prevent folding and tearing where reductions in diameter are involved.

It is customary to lay out copper jobs and, to less extent, high-copper brasses such as 95-5 and 90-10, with a minimum of diameter reduction. On these draws the starting cup practically equals the finish shell in diameter and most of the cold work is involved in ironing the wall. In processing copper shells, it is desirable to keep the number and temperature of interstage anneals to an absolute minimum. This is due to the tendency for the build-up of abnormal grain growth in the shell bottoms and shoulders which, of course, add to the buffing and polishing costs. In the annealing of the oxygen-containing tough-pitch copper shells, care must be taken to guard against hydrogen embrittlement where bright or atmosphere anneals containing varying amounts of hydrogen are being used.

When drawing yellow brass, with its higher strength, it is found possible to obtain substantial diameter reductions, as well as wall reductions, before reannealing is found necessary. Brass jobs are usually laid out with about a 45 per cent reduction of area from blank to cup and with about 30 per cent redraw reductions between anneals, although ideally a decreasing ratio in redraw reductions is desirable; for example, a ratio of 3½, 3½, 3, 2. The use of a good wall reduction on every draw, especially on the last, is important in order to minimize internal stresses. High internal stresses result from draws that involve severe diameter reductions and a minimum of wall reductions. These stresses, when present in yellow-brass shells, cause them to be susceptible to season cracking or stress-corrosion cracking if the shells are not given a final relief anneal.

The harder, more refractory copper-base alloys, such as the phosphor and silicon bronzes, are also readily drawn. However, good gage control on these alloys requires less severe reductions than are used on brass, and bright annealing facilities to minimize abrasive oxides should be available.

A cupping operation may be performed in a double-action press where the outer punch cuts the blank and provides blank holding pressure, or in a single-action press with holding pressures provided by rubber pads. Heavy-gage cups, such as cartridge-case cups, are made in single-action presses without blank holders. Blank holding pressures, when used, must be sufficient to prevent wrinkling but not so tight as to resist the natural thickening of the flange that takes place during cupping. This latter condition may result in thinning of cup bottoms and eventual failure.

Die and punch radii must not be too sharp and dies must be kept well polished. Die radii are generally 5 to 10 times the metal gage. Punches are not polished and may actually be roughened to preserve metal control.

Redrawing is performed in single-action presses and, in the case of yellow brass, reductions of about 30 per cent are involved. These redrawing operations may include heavy wall reductions and light diameter reductions or vice versa, starting with appropriate heavy or thin-gage blanks. Usually, however, the draw involves a combination of these two conditions.

On lighter-type cupping operations and on redraw operations, the best lubricants are various concentrations of soap solutions. With heavy cups, soap pastes containing solids, such as talc, may be found necessary. Ease of removal is an important factor in the use of all of these lubricants.

Press Operations Involving Bulging

Copper and brass articles, such as pitchers and shaker tops, may be subjected to expanding operations known as bulging. Annealed straight-wall shells are expanded up to 30 per cent and much further if performed in two or three operations with intermediate anneals.

This type of operation is usually performed in a suitable mechanical press, using one of three methods. The first of these methods makes use of a segmented steel die and is considered best from a production point of view. In this operation, the shell, placed in the die, is bulged on the down stroke of the press by an expanding insert. The use of these segmented dies may leave objectionable marks on the shell walls.

On small production jobs, rubber punches may be substituted for segmented dies if the die arrangement is such as to enclose the piece being expanded. The rubber punches, made from cylindrical rubber, must be replaced every 2,000 pieces.

For very intricate shapes, hydraulic methods using oil, soap-water, or small steel bulbs are used. However, this type of bulging is fussy and difficult to control with regard to volume and pressure. A fourth method of bulging makes use of a spinning lathe, spinning the bulge inside with a forming roll.

Tapering and Necking Operations

Tapering or necking as a cold-working operation may involve reducing the circumference of drawn shells or rolling one end of a tube to a smaller diameter. The first type of operation is performed in a redraw die and the second type in a rotary swaging machine.

Typical of tapering operations is that performed on brass and steel cartridge cases. For all except slight tapers, the tapered section must be in a soft annealed condition. Where one end of the shell must be kept hard and the taper involves only part of the shell, the anneal used is a controlled end-anneal performed in a salt bath or open gas flame. On severe tapers, a series of operations and anneals may be used.

Cold-working Operations Involving Spinning

For small lots of shells of rotational symmetry, spinning operations may be found more economical than drawing, especially with regard to the initial cost and the maintenance of equipment. The equipment used consists of a spinning lathe of speeds ranging from 1,200 to 2,400 rpm; chucks of wood, cast iron, or chrome-plated steel; and various forming tools and forming rolls of steel or bronze.

In the spinning operation itself, the metal blank to be spun is clamped between the chuck and the revolving tail spindle of the spinning lathe, a hardwood pad (backwood) being attached to the tail spindle. If the shape of the part to be spun does not allow removal of the chuck, sectional chucks that come apart are used. The spinnings are made by gradually pressing the sheet-metal disks over the form as it revolves until the metal fits snugly to the finished shape. Simple-shaped shells require one spinning operation, but more intricate shapes may require several progressive spinnings, possibly with intervening anneals.

Although aluminum is considered the easiest metal to spin, soft-tempered copper, brass, and bronze, up to ¼ inch thick; stainless steel, monel, and "Inconel" up to ⅛ inch; and low-carbon steel up to $\frac{3}{16}$ inch are used in industrial spinnings. Finish-dimension tolerances on spinnings are not so precise as on stampings and die castings, but they are better than on sand castings. Tempers on all metals used for spinning are well on the soft side, in the case of brass running around a soft 0.045-mm grain size. Copper is ductile enough to take extreme spun shapes without annealing, but other copper alloys, such as gilding metal, red brass, yellow brass, and nickel silver work harden faster and require annealing.

Beading and Flanging Operations

Beads are applied to hollow cylindrical shells, such as cans, for both ornamental and strengthening purposes. Beading is done by several methods, the simplest being by means of rolling. A series of beading and flanging operations may be combined on machines equipped with properly shaped arbors and rolls on parallel shafts. A heavy spring may be incorporated in the mechanism to assist in moving the upper shaft over side seams in beading work.

A second method of beading makes use of segmented dies similar to those used in bulging. These segmented steel dies which expand the beads are actuated by wedges, cams, or toggles, and there may be external contracting outside dies for increasing the sharpness of the bead outlines. There is a third method, used for slighter beads on straight tubes or shells. These beads are formed by end thrust imposed on one end of the tube with the lower part held in a closely confined die. In this method, it is desirable for the metal gage to be relatively heavy compared to the outside diameter.

Flanging is similar to beading, using similar equipment and tools. It is used primarily in cylindrical and rectangular can-making, previous to double seaming the can ends. The most obvious method of flanging by drawing only part way through a die is usually not practicable. The usual methods of flanging, like those of beading, involve the use of a series of progressive flanging rolls; expanding and contracting steel dies; or possibly end-thrust methods with endwise die motions like curling.

Impact Extrusion and Cold Extrusion by the Hooker Process

Both of the above operations are applicable to copper and brasses, especially to copper. All types of copper can be cold extruded, but OFHC or phosphorus-deoxidized copper, showing highest ductility, is most extrudable. All of the brasses can be impact extruded into deep thin-wall shells, but increasing difficulties are encountered as the zinc content increases.

Impact extrusion was developed originally for making thin-wall heavy-bottom collapsible tubes out of the softer metals. A thick blank or slug cut from bar stock or sheet is placed in a die of suitable shape. The stock is usually supplied hard to facilitate cutting or blanking, but after annealing the blanks must be carefully cleaned. A punch, of a shape corresponding to the inside of the finished shell, is forced at high velocity into the blank, causing the metal to flow up the side of the punch. A deep thin-wall shell is formed in a single operation, eliminating a number of draws and anneals ordinarily required. This method is also amenable to thin-wall rectangular shells.

Impact extrusion requires robustly built crank presses and special means may be taken to increase ram speed to obtain deeper extrusions. Punch pressures used are very high, ranging from 40,000 psi for lead and tin, 150,000 psi for aluminum, and still higher pressures for copper and brass.

The Hooker process of cold extrusion is a double process involving relatively lower pressures. This process seems more amenable to copper and brass. It enables a deeper shell to be obtained than with regular impact extrusion with the use of less power and less tool wear.

In this process, a thick-walled cup or shell, usually annealed, is fed into a sleeve, a few thousandths larger than the shell. Directly underneath the sleeve is an extrusion die of correct diameter. The descending punch has a diameter fitting into the shell and also a shoulder equal to the outside diameter of the shell. The shoulder of the punch exerts pressure on the open end of the shell and extrudes it through the smaller opening between the punch and die. The extrusion punch is then withdrawn, the die swung underneath a trimming punch, and the shell severed from the small residue, leaving a cleanly cut top.

In this manner, copper, due to its low rate of work hardening, is extruded into deep shells in one operation. It is particularly adaptable for the manufacture of copper tubes. Also, alpha brasses can be extruded into deep thin-wall shells by this process. It is being used as the first operation for deep-drawn shells for the manufacture of small arms ammunition cartridge cases by repeated extrusion and in the production of rectangular shells.

Roll Threading and Knurling

Roll threading is used extensively on solid or heavy-wall cylinders or slugs of various copper and copper-base alloys. However, when leaded alloys such as screw-machine rod are used, some modifications of temper, processing, or alloy may be necessary when the threading or knurling is at all severe. These modifications may involve the use of lighter tempers than in the case of cut-thread operations, or possibly the use of lower-leaded alloys. The more refractory copper-base alloys, such as aluminum bronze, manganese bronze, or silicon bronze, may offer some difficulties in these operations.

There are two methods of roll threading in use. In the first of these, a slug of proper size is placed between two flat hardened steel dies, each provided with parallel grooves which are cut the size and shape of the thread. One die is held stationary while the other reciprocates and rolls the slug between the dies. The other process employs three grooved rollers or cylinders held in a radial position in a rotating die head. The cylindrical dies open up to admit the stock and then close to roll in the thread.

Threads formed by rolling are stronger, smoother, and more uniform than cut threads, but possibly not as accurate. This strengthening results from the fact that the dies are actually forced into the metal while the metal in turn is formed to make the thread tops. Difficulties in roll threading may involve unsatisfactory broken threads or low tool life. The origin of any of these difficulties may be found in the rod being too hard or having too high a lead content. Other possible causes of difficulties may lie in too large a blank or slug diameter or in some tool aberration. In order to counteract brassing and welding, special rolling tools with ground threads and flash chrome-plate surfaces may be employed.

Thread rolling may also be employed on thin-gage drawn shells, using rolls and arbors. A typical example of this is the threaded screw shell for lamp sockets made from copper, gilding metal, and yellow brass. Imposing this thread by means of arbors and rolls on the outside of a hard cup wall may result in high internal stresses. In the case of yellow brasses, this may necessitate a relief anneal.

Knurling is a process similar to roll threading in which a design *instead of a thread is impressed on a solid or hollow metal article. Both* knurling as well as roll-threading operations may be combined with machining operations in an automatic screw machine. Knurling, in the case of leaded brasses, may require a special temper in order to obtain a satisfactory knurl.

Cold Heading and Extrusion

Cold heading is a special form of upset forging in which a head is formed on a piece of wire or rod. In the manufacture of cold-headed rivets, the wire is fed into the header by means of pinching rolls to the correct length. The blank is then cut off and is transferred by a finger to a position in front of the die in a single operation. The blank is then subjected to one or more heading strokes. Sufficient pressure is applied on the end of a slug or cut-to-length piece, forcing the other end into the die and causing a thickened or flanged head of desired shape. The headed rivet is ejected by a knockout pin forming the bottom of the die.

Two types of heading operations are used. In a single-die, two-stroke header, one die is served by two punches supplying two consecutive strokes to the work. In a multidie operation, single-stroke headers are used. After each stroke, the stock is transferred to another die by means of fingers. By this means several rivets in different stages of development are simultaneously headed and otherwise worked.

In present-day headers, a preliminary extrusion operation can be performed by driving the end or point of the shank into a die hole of smaller diameter. This results in a proportionate increase in length and also in strength of the shank, while leaving the remainder of the slug soft enough for the heading operation.

The nonleaded high brasses are especially suitable for cold-heading operations and they generally can be upset about three diameters. Tempers of yellow-brass wire for heading vary from 7 to 40 per cent, depending upon the severity of the heading operation. The temper of wire intended for machine rivets varies from 10 to 20 per cent, but smaller-headed wood screws may require up to 40 per cent hard wire to provide a shank of sufficient strength. When extrusion is a part of the operation, lighter tempers down to 7 per cent hard may be necessary. A certain amount of columnar strength is necessary in the wire used in cold-heading operations.

Low brasses can be upset more than the three diameters found possible in yellow brass, as can the 2 per cent Type B silicon bronze. Both of these alloys also provide good corrosion-resistant products and silicon bronze headed products show good strength. Leaded brasses containing less than 2 per cent lead are limited to 2½ diameters and those containing more than 2 per cent lead to 1½ diameters, as is the case with naval brass.

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Chapter 30

Heat Treatment of Copper and Copper-Base Alloys

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Heat treatment is defined as a combination of heating and cooling operations, timed and applied to a metal or alloy in the solid state in such a way as to produce certain desired properties. Heating for the sole purpose of hot working is excluded from this definition.

Types of Heat Treatment

Copper and brass mill products require four types of heat treatment, as follows:

(1) Annealing for the purpose of softening a cold-worked structure. This is accomplished by heating for recrystallization and grain growth.

(2) Heating for stress relief to prevent season cracking from residual stresses. This is accomplished at temperatures below those causing recrystallization and consequent softening of the metal.

(3) Homogenizing is for the purpose of solution and absorption of segregation and coring found in some cast and hot-worked materials. The common alloys requiring this treatment contain tin and nickel and homogenizing will have been accomplished in the mill before shipment to the fabricator.

(4) Solution treatment and precipitation hardening is a heat treatment applied to a special type of copper alloy. The most common of these alloys contains up to 2 per cent beryllium and may be combined with small amounts of nickel, cobalt, or chromium. These alloys and their heat treatment are specialized and will not be referred to again except in the bibliography.

Annealing Standards

Annealing for the purpose of softening a cold-worked structure will produce different degrees of softening or temper as the temperature and time of heating are increased. For copper and brass mill alloys, grain size is the standard test for annealed material which has been previously cold worked. The standards of the American Society for Testing Materials of Wrought Copper and Copper Alloys list twenty specifications in which grain-size requirements on annealed materials are described. A typical specification contains the following statement: "Grain size shall be the standard for plate, sheet, and strip brasses of all thicknesses in annealed temper, and acceptance or rejection shall depend on grain size." Rockwell hardness values are also given for convenience in testing; they should be considered only as approximate and informatory.

Tables 30-1 to 30-6 give an indication of the type and scope of the ASTM specification for alloys and tempers contained in the ASTM publication by Committee B-5 (1951)[1].

Other ASTM grain-size specifications cover wire and tube products in the regular alloys as well as specialized alloys of copper-nickel-zinc and copper-silicon.

Determination of Grain Size

The American Society for Testing Materials designation E79-49T describes methods for estimating the average grain size of wrought copper and copper-base alloys in an annealed condition. Included therein is a series of twelve photomicrographs of 70-30 copper-zinc alloy which are here reproduced by permission of ASTM (see Figure 30-1).

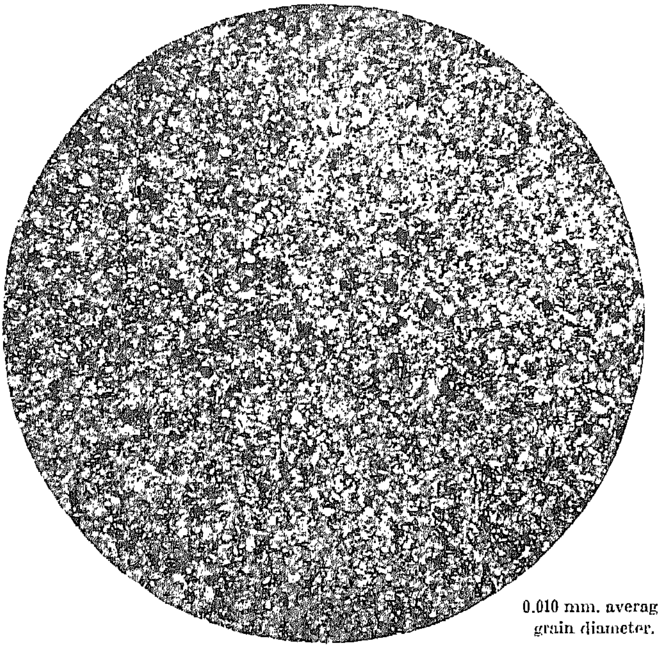
Grain-size measurement is the standard test for wrought materials in an annealed condition because it is a better indication of temper than other mechanical tests such as tensile strength, elongation, reduction of area, or Rockwell hardness.

Correlation with Mechanical Properties

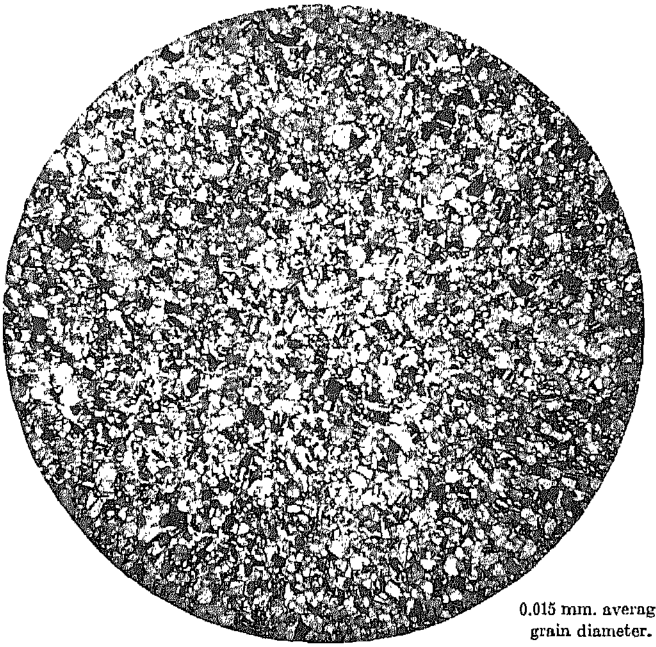
The relationship between grain size and cold workability for copper and copper-base alloys is shown in Table 30-1. This table is more particularly applicable to the lower copper brass alloys such as 65-35 and 70-30. The higher copper alloys are more ductile and do not harden so rapidly with cold work. The 0.035-mm nominal grain size is generally acceptable for deep drawing of these high copper alloys.

TABLE 30-1. GRAIN SIZE FOR COLD WORKING ANNEALED COPPER ALLOYS[2]

Nominal Grain Size, mm	Typical Use
0.015	Slight forming operations
0.025	Shallow drawing
0.035	For best average surface combined with drawing
0.050	Deep drawing operations
0.070	Heavy drawing on thick gages

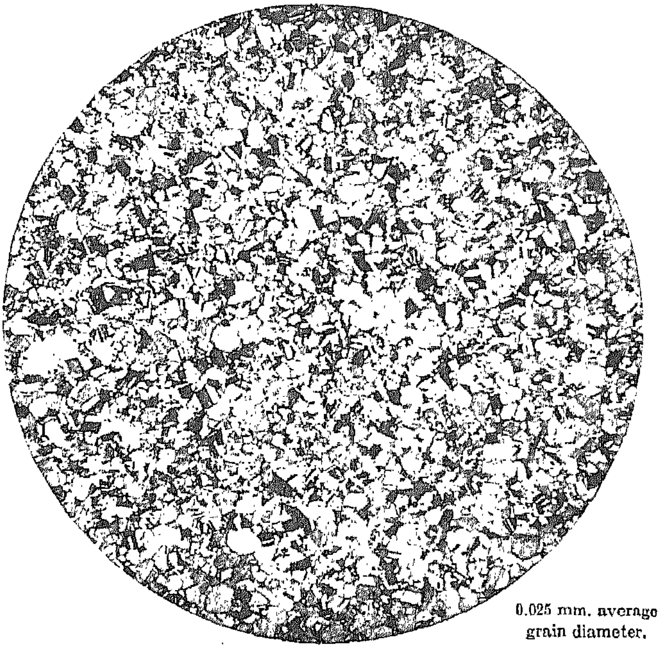


0.010 mm. average grain diameter.

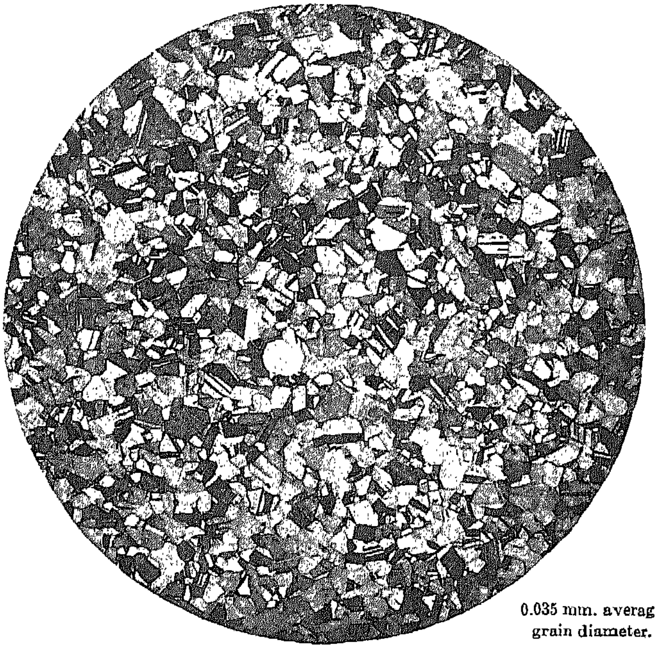


0.015 mm. average grain diameter.

FIGURE 30-1. Grain-size standards for estimation of the diameter of the average grain of annealed wrought copper and copper-base alloys. The micrographs are of 70-30

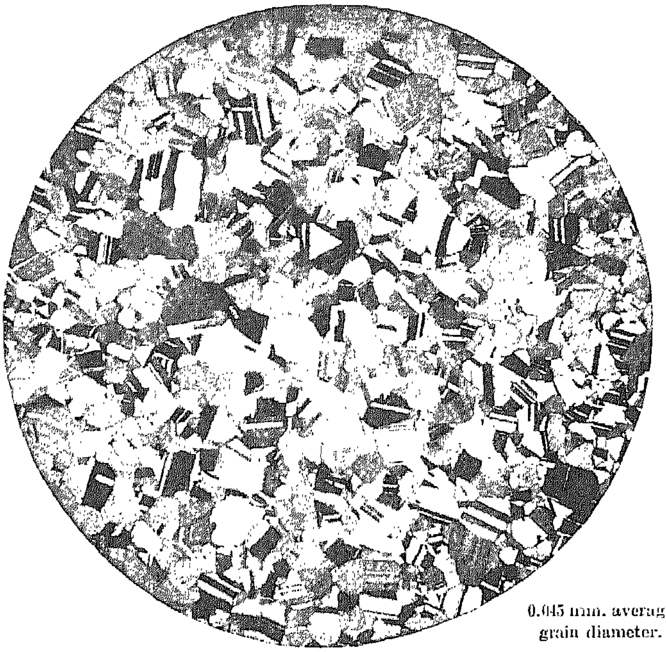


0.025 mm. average grain diameter.

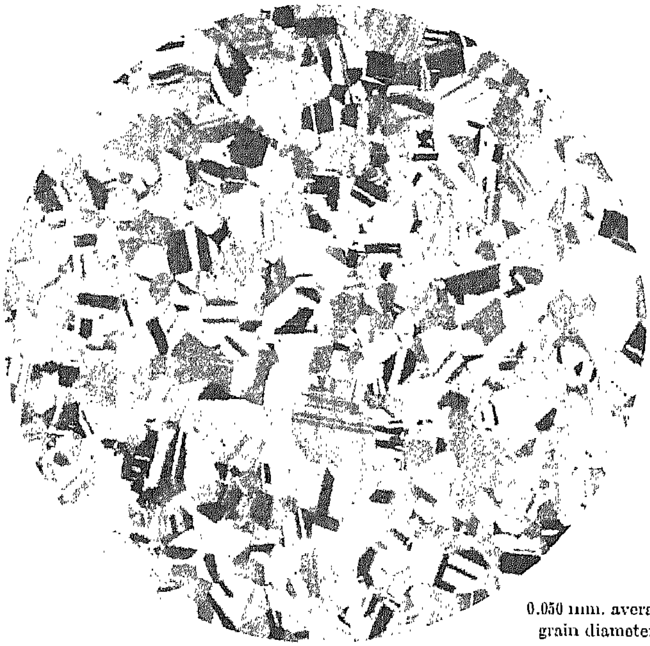


0.035 mm. average grain diameter.

copper-zinc alloy, etched with ammonia and hydrogen peroxide. Magnification 75X. (*By permission of the American Society for Testing Materials.*)

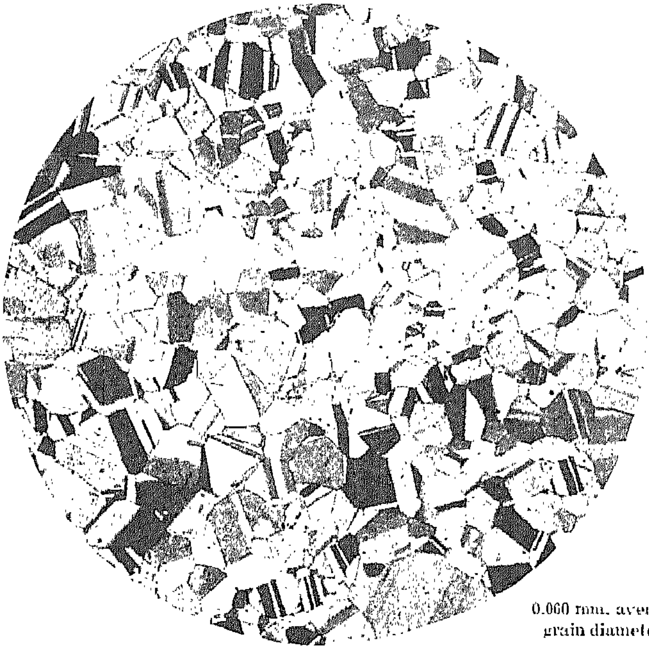


0.045 mm. average grain diameter.

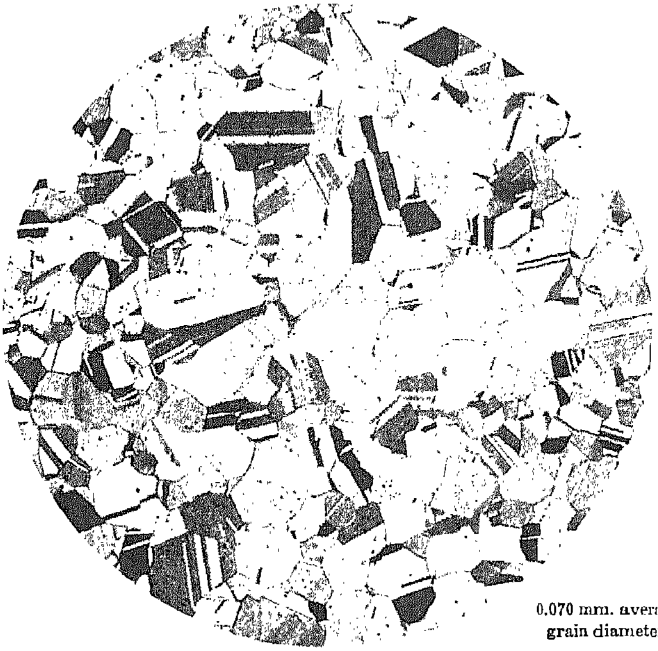


0.050 mm. average grain diameter.

Figure 30-1 (*cont'd*)

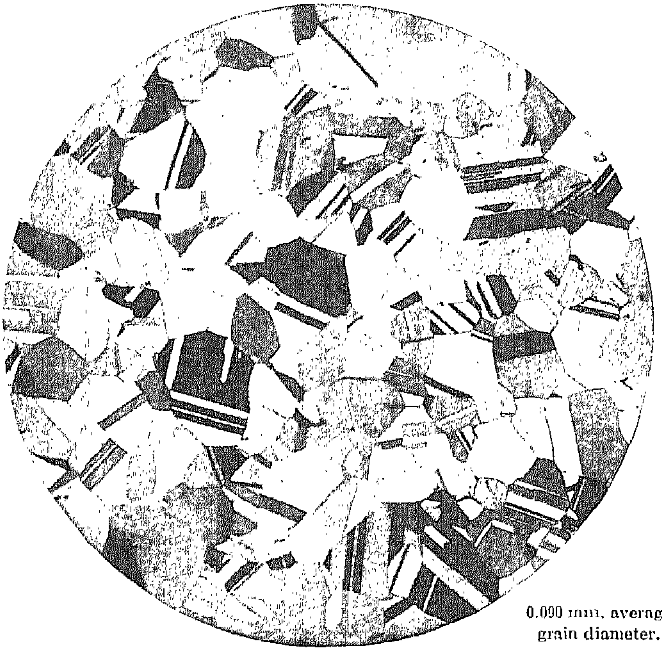


0.060 mm. average grain diameter.

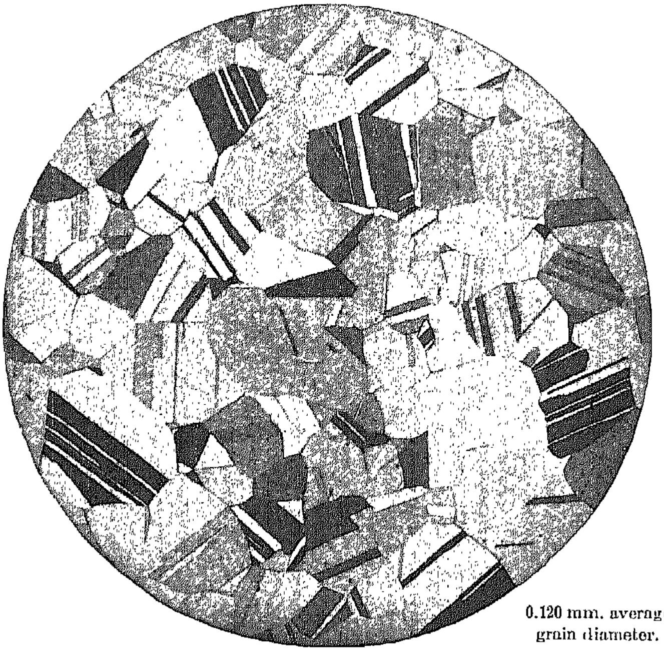


0.070 mm. average grain diameter.

Figure 30-1 (*cont'd*)

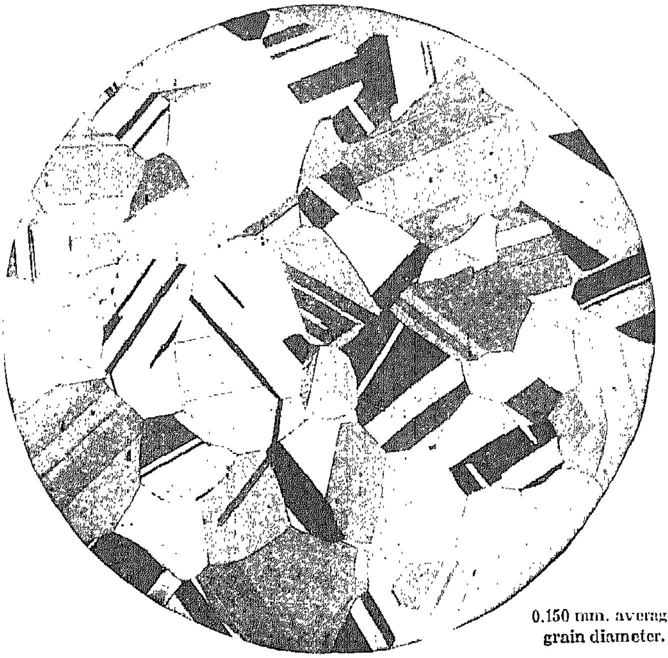


0.090 mm. average grain diameter.

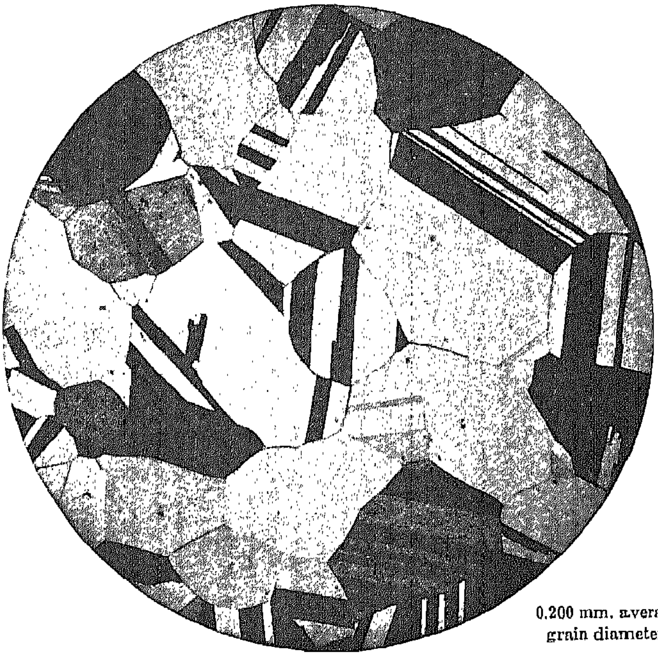


0.120 mm. average grain diameter.

Figure 30-1 (*cont'd*)



0.150 mm. average grain diameter.



0.200 mm. average grain diameter.

Figure 30-1 (*cont'd*)

Burghoff has published a correlation between grain size and mechanical properties of cold-worked annealed copper and copper alloys, from which *Figures 30-2, 30-3, 30-4,* and *30-5* are taken[3].

TABLE 30-2. GRAIN-SIZE REQUIREMENTS FOR COLD-ROLLED ANNEALED TEMPERS, COPPER SHEET, STRIP, AND PLATE

Temper	Grain Size, mm		Rockwell Hardness[b] (Values Included as Information Only)			
			F Scale		Superficial 15-T	
	Min.	Max.	Min.	Max.	Min.	Max.
Soft anneal	a	....	....	65	....	68
Deep-drawing anneal, (0.025 mm nominal)	a	0.050	30	75	44	73

[a] Although no minimum grain size is required, this material must be fully recrystallized.
[b] *Rockwell hardness values apply as follows: The F scale applies to metal 0.020 inch and over in* thickness. The superficial 15-T scale applies to metal 0.015 inch and over in thickness.

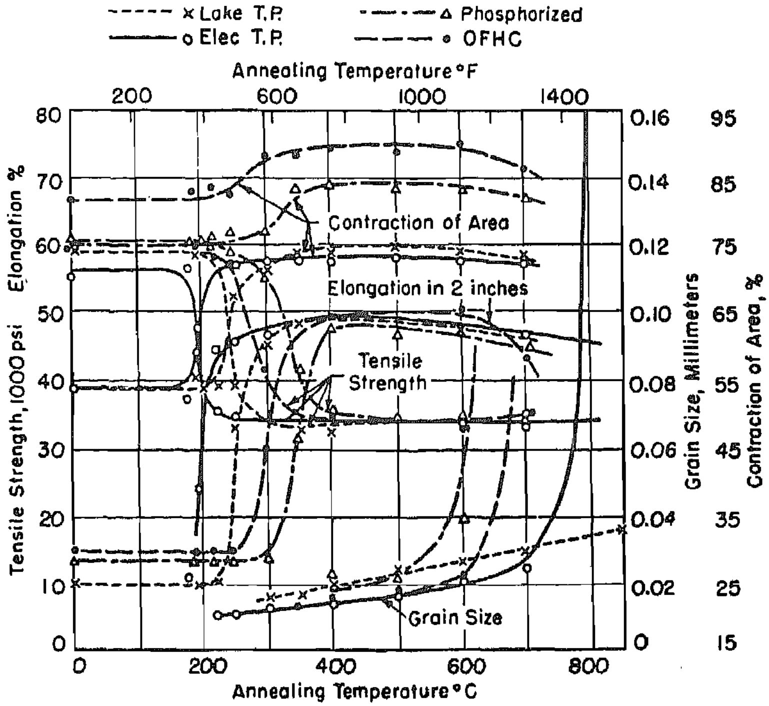


FIGURE 30-2. Effect of annealing on the tensile properties and grain size of tough-pitch Lake, tough-pitch electrolytic, phosphorized (0.02 per cent P), and Oxygen-Free High-Conductivity copper. Wires cold drawn to 62.5 per cent reduction in area and annealed 1 hour. Tested at room temperature.

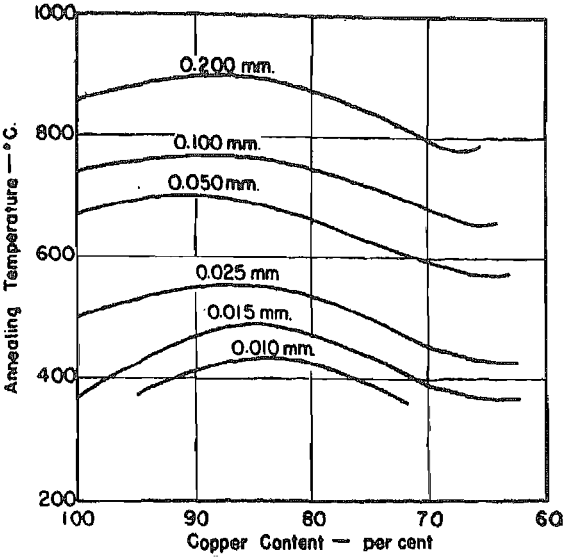


Figure 30-3. Correlation of composition, annealing temperature, and grain size for copper-zinc alloy strip, previously cold rolled to 44 per cent reduction and then annealed 30 minutes.

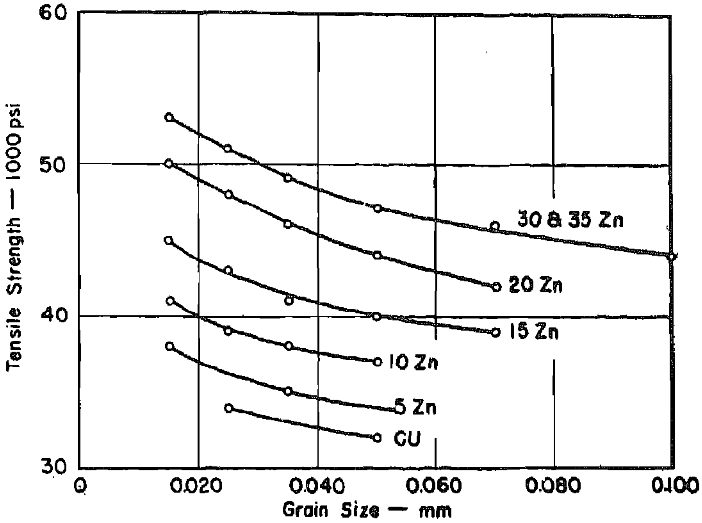


Figure 30-4. Effect of grain size on tensile strength of annealed 0.040-inch strip of copper and brasses of designated zinc contents.

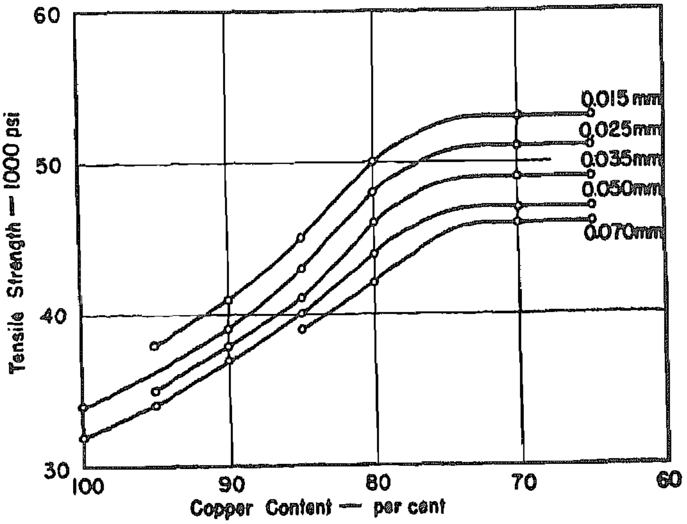


FIGURE 30-5. Tensile strength of 0.040-inch strip of copper and brasses of different copper contents annealed to designated grain sizes.

TABLE 30-3. GRAIN-SIZE REQUIREMENTS FOR ANNEALED PLATE, SHEET, AND STRIP BRASSES

Alloy (For nominal compositions, see Table 30-4.)	Grain Size, mm		
	Nominal	Minimum	Maximum
No. 1	0.050 0.035 0.025 0.015	0.035 0.025 0.015 *a*	0.090 0.050 0.035 0.025
No. 2	0.050 0.035 0.025 0.015	0.035 0.025 0.015 *a*	0.090 0.050 0.035 0.025
No. 3	0.070 0.050 0.035 0.025 0.015	0.050 0.035 0.025 0.015 *a*	0.100 0.070 0.050 0.035 0.025
No. 4	0.070 0.050 0.035 0.025 0.015	0.050 0.035 0.025 0.015 *a*	0.120 0.070 0.050 0.035 0.025
Nos. 6 and 8	0.120 0.070 0.050 0.035 0.025 0.015	0.070 0.050 0.035 0.025 0.015 *a*	...... 0.120 0.070 0.050 0.035 0.025

[a] Although no minimum grain size is required, this material must be fully recrystallized.

TABLE 30-4. APPROXIMATE ROCKWELL HARDNESS OF ANNEALED PLATE, SHEET, AND STRIP BRASSES

Annealed Temper, Nominal Grain Size	Rockwell Hardness[a] (Values Included as Information Only)			
	F Scale		Superficial 30-T	
	Minimum	Maximum	Minimum	Maximum
ALLOY No. 1 (95 Cu, 5 Zn)				
0.050-mm	40[b]	52[b]	....	4
0.035-mm	47[b]	54[b]	....	7
0.025-mm	50	61	1	17
0.015-mm	54[b]	65[b]	7	23
ALLOY No. 2 (90 Cu, 10 Zn)				
0.050-mm	50	60	1	16
0.035-mm	54	64	7	21
0.025-mm	58	70	13	31
0.015-mm	62	75	19	39
ALLOY No. 3 (85 Cu, 15 Zn)				
0.070-mm	53	60	6	16
0.050-mm	56	63	10	20
0.035-mm	58	66	13	24
0.025-mm	60	72	16	34
0.015-mm	62	79	19	48
ALLOY No. 4 (80 Cu, 20 Zn)				
0.070-mm	53	64	2	21
0.050-mm	57	67	8	27
0.035-mm	61	72	16	35
0.025-mm	63	77	20	42
0.015-mm	66	83	25	50
ALLOY No. 6 (70 Cu, 30 Zn) AND ALLOY No. 8 (65 Cu, 35 Zn)				
0.120-mm	50	62	....	21
0.070-mm	52	67	3	27
0.050-mm	61	73	20	35
0.035-mm	65	76	25	38
0.025-mm	67	79	27	42
0.015-mm	72	85	33	50

[a] Rockwell hardness values apply as follows: The F scale applies to metal 0.020 inch in thickness and over; the 30-T scale applies to metal 0.015 inch in thickness and over.

[b] This alloy in these several annealed tempers is too soft for Rockwell F hardness tests below 0.030 inch in thickness.

Heating for Stress Relief

Cold-worked copper alloys such as drawn tubes, rods, and cups are susceptible to season cracking at ordinary temperatures and atmospheres[4]. This type of failure is accelerated in atmospheres containing ammonia.

Failure of this type is most common in alloys containing more than 10 per cent zinc. Naval brass and some aluminum brasses are especially susceptible.

The standard method for determining the presence of residual (internal) stresses which might bring about failure of the material through service or in storage through season cracking is described in ASTM designation B154-50[5].

Relief of internal stresses is accomplished by proper heating or by mechanical flexing. Frequently, a combination of both mechanical and thermal treatment is the most effective method.

Heating for stress relief is done slowly and uniformly at temperatures below the recrystallization temperature. Wilkins and Bunn[5a] have published data which show approximate recrystallization temperatures for copper and the various copper-base alloys. Recommended heating rates are shown in the chapter on "Relief of Residual Stress[6]," in "The Metals Handbook," 1948.

Mechanical flexing may be accomplished by passing the material through the various types of machines used for straightening or flattening rod, tubes, plates, and sheet.

Homogenizing

Homogenizing is defined as a heat treatment, usually for a long time at a high temperature, to eliminate or decrease chemical segregation by diffusion. The common alloys of copper-zinc do not exhibit much segregation or coring above 70 per cent copper. The commercial alloys from 70 per cent down to 58 per cent copper exhibit increasing amounts of the secondary phase segregated in the cast material.

Copper-tin alloys commonly used, containing up to 8 per cent tin, segregate seriously in the castings on cooling through the freezing range. Special homogenizing treatment for many hours at 760°C (1400°F) is necessary before the cast metal can be cold worked without cracking[7].

It is beneficial to use homogenizing treatment for copper-nickel and copper-nickel-zinc alloys where the cored type of segregation is observed in the castings. In all the common brass mill alloys, repeated annealing is necessary for cold working the material to finished sizes. These repeated anneals remove all evidence of segregation in the finished product.

Solution and Precipitation Heat Treatment

A number of commercial copper alloys respond to solution treatment and precipitation hardening. They are of the special type containing beryllium[8]. Precipitation hardening is discussed in Chapter 26 with reference to aluminum-copper alloys (see page 574).

Type of Furnace

Choice of furnace type depends upon the material to be annealed. The shape and weight of each piece and the total quantity in pounds per hour affect the type of furnace required. The material must be handled so that no damage to the surface occurs, such as dents, scratches, or distortion. Protective atmospheres may be used as required.

The Continuous Furnace. This type of furnace is well adapted to a steady flow of work. Light loads may be handled on mesh belts; heavier loads directly or in trays on skids or rollers, using pushers or driven rolls. Some continuous furnaces have a rotary hearth and may be charged and discharged through the same or adjacent doors. Another variation of the continuous furnace is the strip or strand furnace wherein a strip of sheet metal or a strand of wire, either singly or in multiple, is pulled through a vertical or horizontal furnace. The strip or strand furnace may be augmented by a cleaning and pickling unit, in tandem, which produces annealed and cleaned material in one operation.

The advantages of continuous furnaces lie in providing a steady flow of work. Generally light loads, one unit high, are used, aiding greatly in producing uniformity of heating. Because of light loads, the heating time is relatively short, which is especially beneficial when controlled atmospheres are employed for bright or clean annealing.

The disadvantages of continuous furnaces are associated with time lost in loading and emptying the furnace when starting or stopping or when changing temperatures or time of travel through the furnace. The continuous furnace is not ideally suited to jobs that do not run steadily at the same temperature and heating time.

The Batch-type Furnace. This is especially advantageous when running a variety of work requiring many changes in temperature, heating time, or method of loading. Protective atmospheres may be used, but a suitable cover is needed to protect the work while heating or while cooling to room temperature. Batch furnaces may vary in size from 6-inch boxes to freight-car dimensions or larger. The furnace may be box, round, pit, or bell shaped with fixed hearth, movable roller hearth, or car-bottom hearth. The batch furnace is fully loaded in one operation, using a suitable handling device such as a tray, bucket container, handling forks on a special crane, car-bottom hearth, or other means. After the load is heated and soaked at temperature, it is unloaded and the furnace is ready for the next charge.

The Bell-type Furnace. The bell-type furnace is a variation of the batch type in which work is loaded on a stand and the furnace lowered over the work. One furnace can service several stands. For example, using protective atmospheres, one furnace is used with four stands. One stand is loading and purging, the second is heating, and the third and fourth are cooling to safe temperatures for removal of the protective cover and unloading. This type of furnace is especially well adapted to the use of protective atmospheres, since the cover may be readily sealed with oil and water traps.

The Intermittent Roller-hearth Furnace. Another variation of the batch furnace which is much in use in brass mills is the intermittent roller-hearth furnace. A roller-hearth conveyor is used to advance the work from loading station to purging chamber, to heating chamber, and thence to cooling chamber and unloading stations. The roller conveyor in the heating and cooling chambers oscillates a distance approximately equal to the circumference of the rolls, thereby preventing distortion of the rolls due to the weight of the load or nonuniform roll heating.

The advantages of batch-type furnaces lie in the reduced floor area required, and their adaptability to a wide variety of work requiring different temperatures, loads, or time cycles. This provides a flexibility difficult to attain with continuous furnaces.

The disadvantages of batch furnaces are associated with "in" and "out" operation and difficulty in loading. Uniformity in heating to temperature throughout the load can be obtained only at a considerable sacrifice in production rates. Longer periods required for heating and cooling adversely affect bright and clean annealing in protective atmospheres.

The Salt-bath Furnace. This furnace is generally used in the copper and brass industry for heating a portion of the work such as mouth anneals on artillery cases or the end sections of brass tubing. A pot furnace provides an easy means of heating without oxidation and some protection from oxidation is also provided by the residual salt remaining on the work after removal from the pot. When used at high annealing temperatures the work is sometimes difficult to clean because of the staining of the salt.

Standard for Surface Appearance

There is only one criterion for the surface obtained in heat treatment, that of economy of finishing the material. For example, a sheet of metal having a grain size of 0.050 mm average diameter will exhibit an "orange peel" surface when formed, as shown in Figure 30-6. A nominal grain size of 0.025 mm average diameter is therefore desirable for buffing and polishing operations because less work is required to finish a smoother appearing formed surface. Sometimes it is economical to save on the forming operation by using a larger grain size or softer material, but usually the reverse is true since buffing is the more expensive operation.

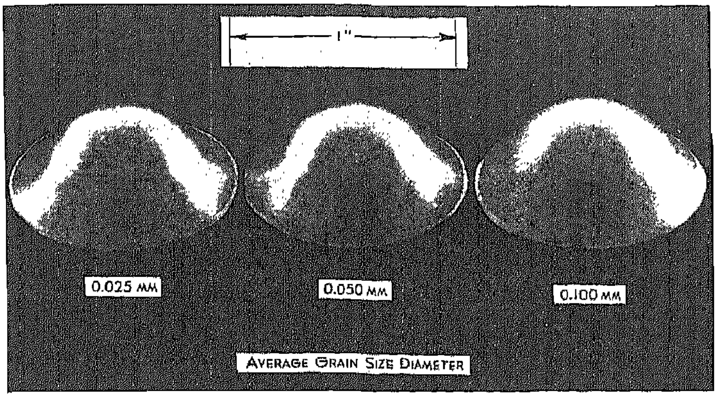


FIGURE 30-6. "Orange peel" surface resulting from drawing operation on sheet metal of too large grain size.

A stained surface is generally etched slightly when cleaned in any of the standard cleaning solutions and consequently will require more work to polish than one which is not stained or etched.

Lubricants used in forming operations frequently stain the work while standing, awaiting heat treatment. They invariably cause some staining during heating. Again it is a question of economy as to whether it is better to put in a cleaning operation before heating or face additional cleaning expense after the material has been heat treated.

Factors Which Affect Annealing and Heat Treatment

Uniformity of temper is the first requirement. It was shown that grain size is the standard measure of temper. A means of selecting the proper temper is given by the nominal grain size recommended for the metal for the type of work to be performed upon it.

The finished surface requirements are next to be considered. To provide the best surface costs money. The finish required determines the type of furnace, fuel, protective atmosphere, and the washing and cleaning methods used before and after heating.

The temperature required determines whether the furnace shall be of light or heavy construction, the kind of fuel, and the type of controls necessary. The temperature also affects the finish. Lubricants used in working the metals will sometimes burn off at high temperatures leaving a deposit which will pickle easily, whereas low temperatures will not burn off the oils completely and it may be found necessary to clean the metal before as well as after heat treating. Low-temperature annealing is a pronounced aid in clean annealing alloys containing zinc.

The time in the furnace is determined by the mass to be heated and the method of loading. Generally, the less time a piece is in the furnace, the cleaner it will be upon leaving. Time required varies with the method of loading. Pieces in a layer one unit high require less heating and cooling time than those in a dense load several layers deep. Forced circulation by fans which move the atmosphere in heating and cooling chambers can reduce time for these operations by as much as 30 per cent.

Protective Atmospheres

Protective atmospheres for bright or clean annealing are used in the furnace to prevent oxidation of the metal annealed during the heating and cooling cycle. Copper and copper alloys which do not contain zinc are relatively easy to bright anneal.

Because copper and copper alloys are not readily oxidized by water vapor or CO_2, protective atmospheres of steam, partially burned gas, and partially burned charcoal have been in use for annealing for many years. It is the writer's belief that steam was first used for bright annealing copper in Connecticut in an English furnace supplied in 1907 by Bates and Peard of Liverpool. By 1913 variations with steam and partially burned gas or charcoal were used in many applications throughout the industry.

During the past 20 years there has been extensive progress in the use of protective atmospheres[9]. In the annealing of steel, water vapor and CO_2 are oxidizing so that equipment has been developed to eliminate these gases. Today in the copper and brass industry there are many installations providing protective atmospheres with CO_2 removed and dewpoints of −40°F. It is necessary to use a muffle-type furnace, or one heated by radiant tubes or electrical resistors, to prevent contamination by sulfur or water vapor in the flue gases.

Alloys of copper and zinc will generally require pickling[10] even after annealing in protective atmospheres because the zinc diffuses to the surface, causing discoloration and a deposit which increases tool wear in subsequent forming operations. This difficulty is magnified by high zinc content, high annealing temperatures, and long periods for heating and cooling. Cartridge brass presents great difficulty in bright annealing.

It is common practice today to process bright or clean annealed material without further pickling and cleaning if the metal is copper, cupro-nickel, phosphor bronze, or other alloy which does not contain zinc. Nickel silver containing 20 per cent zinc is an exception and can be bright annealed in continuous furnaces where the heating and cooling are of short duration.

Sulfur will stain these alloys and must be kept to a minimum. If the work has a dirty surface left from previous oxidation, poor pickling, or processing lubricants, it will surely be dirty after bright annealing. Best results are obtained if the metal is cleaned before it is annealed[11]. Chlorides will stain extensively and while not generally encountered, they may come from some of the cleaning solutions used before or after annealing. If present in the air used for combustion of fuel, no end of trouble will result in an open-fired furnace.

Bright annealing and clean annealing of copper has been accomplished in open-fired furnaces for fifteen years or more. This development was made possible by proper application of dependable proportioning devices for mixing air and fuel. The work must be fed through the furnace at a continuous and fairly constant rate to insure sufficient products of combustion to exclude all unburned air. Protective atmosphere generators to supplement gases from the furnace burners are an effective aid to operation of this type of furnace, particularly when loading or emptying the furnace.

The various types of protective atmosphere generators depend on accurate proportioning of fuel and air and also on the fuel being of constant analysis.

Probably best adapted to the use of protective atmospheres is the bell-type furnace because of the ease of sealing the protective cover. The purging of air before heating and the cooling may be done under the sealed cover independently of the furnace. This makes for an economical installation for handling loads in large batches.

Continuous and semicontinuous furnaces are frequently used where there is an advantage in handling the load continuously.

Composition and cost of producing protective atmospheres and recommendations for the type of atmosphere to be used for heat treating copper and copper alloys are covered in Table 30-5[12].

General Approach to Heating Problems

Reduced to the essentials, the heating problem is always the same. It is to produce the temper required for further working or that best suited to the finished article. How the material is heated depends on the alloy, shape, quantity, uniformity, and finish required and on the furnace in which it is to be heated.

Only the simplest academic types of heating problems can be calculated from data now available. There is a wealth of data for calculating heat flow through furnace walls. There are also formulas, tables, and charts

TABLE 30-5. APPROXIMATE COMPOSITION AND COST OF PRODUCING TYPICAL FURNACE ATMOSPHERES

Item	Furnace Atmosphere	Type of Reaction	Ratio of Air to Natural Gas	Composition, Per Cent						Dew Point, deg Fahr	Cost per M cu ft,[a] dollars
				CO_2	O_2	CO	H_2	CH_4	N_2		
I	Hydrogen	Electrolytic									
	A Unpurified										
	1. From cells		....	0.0	0.2	0.0	99.8	0.0	0.0	Saturated	1.50 to 3.00
	2. From bottles		....	0.0	0.2	0.0	99.8	0.0	0.0	−30 to −10	5.00 to 10.00
	B Purified										
	1. From cells		....	0.0	0.0	0.0	100.0	0.0	0.0	−60	1.52 to 3.02
	2. From bottles		....	0.0	0.0	0.0	100.0	0.0	0.0	−60	5.01 to 10.01
II	Dissociated ammonia	Endothermic									
	A Untreated		....	0.0	0.0	0.0	75.0	0.0	25.0	−60	0.95 to 3.50
	B Burned with air										
	1. Partly burned		1/1	0.0	0.0	0.0	24.0	0.0	76.0	Saturated	0.57 to 2.10
	2. Completely burned		1.75/1	0.0	0.0	0.0	1.0	0.0	99.0	Saturated	0.72 to 2.70
III	Combusted fuel gas	Exothermic									
	A Unpurified										
	1. Partly burned		6/1	5.0	0.0	10.0	15.0	1.5	68.5	Saturated	0.10
	2. Completely burned		10.25/1	11.5	0.0	0.7	0.7	0.0	87.1	Saturated	0.08
	B Purified										
	1. Partly burned										
	a. Dry and free from CO_2		6/1	0.0	0.0	10.5	15.5	1.5	72.5	−40	0.14
	2. Nearly completely burned										
	a. Dry and free from CO_2		9.5/1	0.0	0.0	2.0	2.0	0.0	96.0	−40	0.13
	3. Completely burned										
	a. Dry and free from CO_2		10.25/1	0.0	0.0	0.7	0.7	0.0	98.6	−40	0.13
	b. Converted with charcoal (No H_2O removed)		10.25/1	0.0	0.0	30.0	16.0	0.0	54.0	−15	0.32
	c. Converted with charcoal (H_2O condensed)		10.25/1	0.0	0.0	20.0	3.0	0.0	77.0	−20	0.22
IV	Reacted fuel gas	Endothermic									
	A With air over catalyst										
	1. Completely reacted		2.25/1	0.0	0.0	19.0	38.0	1.5	41.5	−10	0.22

[a] Costs include only materials consumed, such as power, gas and water. They do not include factors for obsolescence, installation, maintenance, and the like. The estimates have been based on the following unit costs: power, 1 cent per kw hr; natural gas, 50 cents per M cu ft; water, 5 cents per M gal; charcoal, 3 cents per lb; ammonia, 3½ to 15 cents per lb.

TABLE 30-6. FURNACE ATMOSPHERES RECOMMENDED FOR ANNEALING

Metal to Be Annealed	Surface	Temp. Range, Deg. Fahr.	Furnace Atmospheres Recommended
Copper	Bright	500 to 1200	III A2
Copper-nickel	Bright	800 to 1400	III A1, I A1, I A2, II B1
Brass	Clean	800 to 1400	III A2, III B3a

which will aid in estimating the heating time in "steady state" for various degrees of uniformity in such basic shapes as spheres, plates, or cylinders of indefinite length[13]. Even these calculations are tremendously influenced by variable values for conductivity, emissivity, and forced convection. The theoretical solution may be many times away from the exact answer because of wrong selection of values for the variables.

Until there are more data available, actual experience of the user aided by the experience of the furnace builder will produce the best result by repeated trials. Anyone familiar with furnaces heating similar pieces of work can make a close assumption of heating time required for uniformity. The furnace builder can make close approximations for capacity and uniformity of new equipment using such rough rules as pounds per square foot of hearth area with empirical allowances for quantity, shape, temperature, alloy, surface emissivity, and forced convection.

Types of Heating Problems

There are two types of heating problems regularly encountered in actual plant practice, as follows:

(1) A new furnace is to be purchased to do a certain job. It may be selected to do a single job or to be able to do a variety of similar work.

(2) A furnace which was designed for a certain job is ready and available in the plant, but now must also do a new type of work.

The second problem is the one which most frequently perplexes the plant engineer. However, the factors considered in the choice of new equipment are the same as those which must be weighed in adapting existing equipment to a new duty. For this reason, the purchase of a new furnace will be discussed here.

Selection of New Furnace Equipment and Fuel

The first item to be considered in the purchase of new heating equipment is fuel. This is important from the standpoint of economy, availability, automatic control, and sulfur content. Alloys containing appreciable amounts of copper are stained by contact with sulfur in the fuel.

Oil is generally cheaper than gas but presents more of a problem from the standpoint of sulfur. It is not as satisfactory for automatic control because burners are more apt to become fouled and require more constant attention as well as considerably more maintenance. For temperatures below 600°C (1100°F), it is difficult to maintain satisfactory flame control and the resulting smoke is a very real nuisance. Copper and brass mills throughout the country use fuel oil for heating, although its use for final anneals has almost vanished.

The American Society for Testing Materials lists the standard specifications for fuel oils under D-396-48T. This specification allows a sulfur content as high as 0.50 per cent maximum. There is also this important footnote to the specification: "Recognizing the necessity for low-sulfur fuel oils and in connection with heat treatment, *nonferrous metals,* glass and ceramic furnaces, and other special uses a sulfur content may be specified . . . by mutual agreement between purchaser and seller."

Most brass mills would specify about as follows:

Fuel Oil for Billet and Bar Heating Furnaces

ASTM D-396-48T #2 Grade Fuel Oil. Sulfur 0.50 per cent max.

Fuel Oil for Final Anneals

ASTM D-396-48T #2 Grade Fuel Oil. Sulfur 0.20 per cent max.

Gas is more satisfactory than oil because of less burner maintenance and better automatic control, especially at lower furnace temperatures. The latter is particularly true for stress-relief heating where furnaces sometimes operate at temperatures as low as 200°C (400°F).

Sulfur is also a problem with manufactured gas and the lower the sulfur, the better the finished surface. It is claimed that sulfur when completely burned in an open furnace will not stain copper or copper-base alloys. Many furnaces now in use are fired by open flames in the furnace chamber.

Propane and butane liquefied petroleum gases are in wide use today and are quite satisfactory. Propane may be obtained with sulfur content under 6 grains per hundred cubic feet of gas.

Radiant tube burners may be used with gas-fired furnaces. The burners fire into tubes extending through the furnace heating chamber. The products of combustion do not enter the furnace and the result is similar to an electric heating element. Forced convection is necessary for uniform heating. The cost is less than for electric power and about the same as for direct-fired gas furnaces. This type of furnace is much used with protective atmospheres in the heating chamber.

Electricity is used for heating quite satisfactorily, but is generally more expensive than gas and oil. There is no sulfur problem with electricity. Forced convection with fans is essential to circulate the furnace atmosphere for uniform heating electrically. Heat is generally supplied through resistance bars inside the furnace.

There are several applications in use for heating brass tubing and fine wire by using the resistance of the material itself to generate the heat required. Induction heating of copper and brass mill alloys is generally confined to applications for brazing and soldering assemblies. Some recent furnaces have been designed for heating billets for extrusion presses.

Determination of Heat Treatment for Specific Purposes

After the furnace has been selected and installed, there is only one sure way to establish the time, temperature, and load concentration required for uniformity of temper. The procedure is actually to record the time intervals and related temperature difference between the surface and center of the pieces heated.

If the piece is large enough to have an appreciable temperature difference between the surface and the center, it is advisable to weld thermocouples at these points and make actual test runs in the furnace, recording time and temperature during heating and soaking. For continuous furnaces, thermocouples with leads long enough to travel with the work from the charging end to discharge end must be used. A load one layer high will heat more uniformly. Since furnaces have hot and cold regions, or at least places in the load which come up to temperature more slowly, the test thermocouples should be placed so that the time and temperature readings will include the complete range of temperatures met with throughout the furnace chamber. Results of these tests should always be checked against the grain size obtained. This method will provide more information than calculation. Such tests provide the best data on work and furnace temperatures on which to base heat treatment.

Softness or grain size in copper and copper-base alloys is a function not only of temperature but of time. This is fortunate because soaking the work at temperature produces the most uniform results.

Figure 30-7 shows that for any final temperature there is little increase in grain size after the first hour[14]. Maximum uniformity of heat treatment for these materials is obtained by soaking the load for at least 1 hour after the last part has come to temperature.

Small objects have little temperature difference between surface and center, so that uniformity may be obtained by holding at temperature for relatively short periods. Strip and strand furnaces hold the work at temperature for only a few seconds.

If the work is always the same, it is possible to maintain excellent uniformity using a light load and short heating time, provided other factors remain constant. Variations due to composition, impurities, lubricants, surface emissivity, gage, heat balance in the furnace, and others are all causes of nonuniformity when short-time cycles are used. Longer cycles, of course, lessen the effect of these variables.

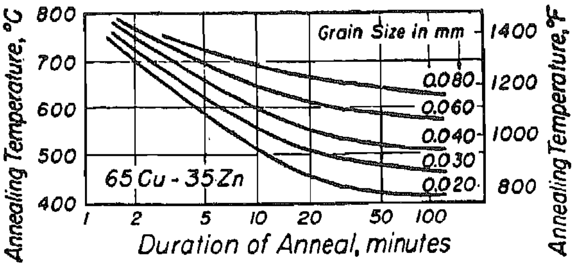


FIGURE 30-7. Effect of time and temperature on annealing of yellow brass strip, 0.050-inch gage. (*After Pratt*[14].)

Uniformity of heat treatment must be balanced against the cost of producing it. The cheapest heat treatment is done with high thermal gradients, heavy loads, and short cycles. It requires smaller investment in furnace capacity per unit weight annealed, and provides quicker turnover of the work. But, in general, it has been found that money spent to insure uniformity and clean surface will be returned by savings in forming and finishing operations.

Acknowledgments

The author wishes to express his indebtedness to Mr. Lyle Carson for his part in editing and criticizing this article, and to members of the Scovill Manufacturing Company Metals Research Department.

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Chapter 31

Machining Characteristics of Wrought Copper and Copper Alloys

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Copper and copper alloys constitute a class of materials that can be machined by many methods although their machining characteristics cover a broad range. Typifying materials of widely varying machinability, there may be cited (a) pure copper, which, although comparatively soft, presents certain difficulties because of its toughness and the stringiness of its chips; (b) the high-strength aluminum bronzes, which resist cutting because of their hardness; and (c) free-cutting brass, which is so widely used for screw machine work because of the extreme ease of cutting it and of clearing the chips from the tool. This variability is occasioned chiefly by chemical composition, with its inherent effects on physical and mechanical properties, plus a slightly modifying effect of temper. It is the purpose of this chapter to discuss these factors, to demonstrate their effects in the numerous commercial copper alloys, and to indicate some of the mechanical factors of speeds, feeds, and tooling.

Alloy Groups

For convenience, one may place all commonly used copper-base materials in three groups with respect to machinability, as follows:

Group I: Free-cutting alloys.
Group II: Moderately machinable alloys.
Group III: Alloys difficult to machine.

This is done in Table 31-1, where the names, compositions, and typical tensile properties of an illustrative list of wrought coppers and copper alloys are presented along with generally accepted machinability ratings.

TABLE 31-1. COMPOSITIONS AND PROPERTIES OF COMMON WROUGHT COPPER AND COPPER ALLOYS

Alloy	Nominal Composition, per cent	Form	Temper	Tensile Strength, psi	Machinability Rating	Type of Chip*
	GROUP I: Free-cutting Alloys					
Leaded copper	Cu 99, Pb 1	Rod	Hard	45,000	80	M
Tellurium copper	Cu 99.5, Te 0.5	Rod	Hard	48,000	90	S
Leaded commercial bronze	Cu 89, Pb 1.75, Zn 9.25	Rod	Half hard	52,000	80	MS
Medium-leaded brass	Cu 65, Pb 1, Zn 34	Rod	Quarter hard	55,000	70	M
High-leaded brass (tube)	Cu 66, Pb 1.6, Zn 32.4	Tube	Hard	75,000	80	S
High-leaded brass	Cu 63, Pb 1.8, Zn 35.2	Rod	Half hard	58,000	90	S
Free-cutting brass	Cu 61.5, Pb 3, Zn 35.5	Rod	Half hard	58,000	100	S
Forging brass	Cu 60, Pb 2, Zn 38	Rod	Hot forged	52,000	80	S
Architectural bronze	Cu 57, Pb 3, Zn 40	Rod	Extruded	60,000	90	S
Leaded naval brass	Cu 60, Sn 0.75, Pb 1.75, Zn 37.5	Rod	Half hard	75,000	70	S
Free-cutting phosphor bronze	Cu 88, Sn 4, Pb 4, Zn 4	Rod	Hard	65,000	90	S
Extruded leaded nickel silver, 10%	Cu 46.5, Ni 10, Pb 2.75, Zn 40.75	Rod	Hard	70,000	80	S
	GROUP II: Moderately Machinable Alloys					
Red brass, 85%	Cu 85, Zn 15	Tube	Hard	70,000	30	L
Low brass, 80%	Cu 80, Zn 20	Strip	Hard	74,000	30	L
Cartridge brass, 70%	Cu 70, Zn 30	Rod	Half hard	70,000	30	L
Muntz metal	Cu 60, Zn 40	Rod	Quarter hard	72,000	40	L
Low-leaded brass (tube)	Cu 66, Pb 0.5, Zn 33.5	Tube	Hard	75,000	60	M
Admiralty	Cu 71, Sn 1, Zn 28	Tube	Soft	53,000	30	L
Naval brass	Cu 60, Sn 0.75, Zn 39.25	Rod	Half hard	75,000	30	L
Manganese bronze (A)	Cu 58.5, Sn 1, Fe 1, Mn 0.3, Zn 39.2	Rod	Half hard	84,000	30	L
Aluminum brass	Cu 76, Al 2, Zn 22	Tube	Soft	60,000	30	L
High-silicon bronze, 3% (A)	Cu 96, Si 3	Rod	Half hard	78,000	30	L
Low-silicon bronze, 1.5% (B)	Cu 97.5, Si 1.5	Rod	Hard	70,000	30	L
Leaded phosphor bronze, 5% (B)	Cu 94, Sn 5, Pb 1	Rod	Hard	70,000	50	M
Leaded nickel silver, 65-12-1	Cu 65, Ni 12, Pb 1, Zn 22	Rod	Hard	68,000	50	M
Aluminum-silicon bronze	Cu 91, Al 7, Si 2	Rod	Soft	90,000	60	M

TABLE 31-1. (*Continued*)

Alloy	Nominal Composition, per cent	Form	Temper	Tensile Strength, psi	Machinability Rating	Type of Chip*
GROUP III: Alloys Rated Difficult to Machine						
Copper, electrolytic tough pitch	Cu 99.90+, O 0.04	Rod	Hard	48,000	20	L
Copper, phosphorized and oxygen-free	Cu 99.90+, P 0.02	Tube	Hard	55,000	20	L
Commercial bronze, 90%	Cu 90, Zn 10	Rod	Eighth hard	45,000	20	L
Phosphor bronze, 5% (A)	Cu 95, Sn 5	Rod	Half hard	70,000	20	L
Phosphor bronze, 8% (C)	Cu 92, Sn 8	Rod	Half hard	80,000	20	L
Phosphor bronze, 10% (D)	Cu 90, Sn 8	Strip	Hard	100,000	20	L
Cupro-nickel, 10%	Cu 89, Ni 10, Fe 1	Tube	Light-drawn	60,000	20	L
Cupro-nickel, 30%	Cu 69.5, Ni 30, Fe 0.5	Rod	Half hard	75,000	20	L
Nickel silver, 65-18	Cu 65, Ni 18, Zn 17	Rod	Half hard	70,000	20	L
Nickel silver, 55-18	Cu 55, Ni 18, Zn 27	Strip	Hard	100,000	20	L
Nickel silver, 65-12	Cu 65, Ni 12, Zn 23	Strip	Hard	85,000	20	L
Aluminum bronze, 5%	Cu 95, Al 5	Tube	Soft	60,000	20	L
Aluminum bronze, 7% (D)	Cu 91, Al 7, Fe 2	Plate	Soft	75,000	20	L
Aluminum bronze, 10% (E)	Cu 82, Al 9.5, Ni 5, Fe 2.5, Mn 1	Plate	Soft	95,000	20	M
Beryllium copper	Cu 97.7, Be 2, Ni 0.3	Sheet	Soft	70,000	20	L
Chromium copper	Cu 99.5, Cr 0.5	Rod	Hard	72,000	20	L

* L=long chip, M=medium chip, S=short chip.

The entries have been taken largely from the "Manual of Standards" of the Copper and Brass Research Association[1], and from "The Metals Handbook[2]," with supplementary data from producers' literature.

The limiting machinability ratings of the three groups must be arbitrary, for the number of alloys to be considered is so great and their properties correspondingly so widely ranging that there are no sharply defined areas of separation as the list goes gradually from free-cutting to difficultly machinable alloys.

Machinability Rating

The significance of the machinability rating should be discussed at the outset, for it is of the essence of this article. It is, however, a term without precise meaning, for there is no simple nor single criterion of machinability. What are integrated into it are practical experience in various cutting operations, the observed rate of wear of cutting tools, the ease of penetration of cutting tools into the alloy as indicated in certain laboratory tests, and the type of chip. As a convenient standard, a machinability rating of 100, or 100 per cent, is commonly assigned to free-cutting brass, which is substantially unsurpassed in the copper-alloy field with respect to the ease with which it may be machined. Alloys which are more difficult to machine are given a rating of less than 100.

It will be noted that the materials of Group III have a common machinability rating of 20. This is partly an indication of ignorance rather than of strict equality of the several materials in the group. It is to be expected that there are real differences in machinability within the group just as there are differences in hardness and strength, even though all the items share the common attribute of great toughness.

The value of the rating is considerable, although largely qualitative. As an index for determining proper speed of work or tool, feed, and rate of wear of tool, it is a first approximation which must be proved by trial and error for a given job.

The type of chip is of itself important and three general types are commonly recognized, as has been pointed out by Crampton[3]. The desirable short chip is characteristic of what may be produced from free-cutting brass with proper tooling. Its brittleness as formed promotes its small size and facilitates clearing of the tools. The chip of moderate length is typical of some alloys of intermediate machinability. Its brittleness is insufficient to produce really short chip formation, but is enough to permit comparatively easy fracture of the chip as formed. The long, tough chip, characteristic of pure copper and numerous nonfree-cutting alloys, is often difficult to handle and may lead to the fouling of tools.

The Effect of Composition

Copper. Copper is comparatively soft, ductile, and tough and these characteristics manifest themselves in machining. Tools penetrate into copper easily, but its toughness demands a high energy for the separation of the chip from the parent stock so that there is a generation of a considerable quantity of heat. The toughness and ductility of the metal account for the long, stringy chips which are formed in most cutting operations.

Of the so-called pure coppers which are marketed, the deoxidized and oxygen-free types are slightly more difficult to machine than the oxygen-bearing, tough-pitch coppers, in which the presence of particles of cuprous oxide appears to offer some measure of improvement. For example, the conversion of heavy-walled copper tube to thin, helical fins for radiators by means of a skiving operation has been found to be easier with tough-pitch copper than with deoxidized copper.

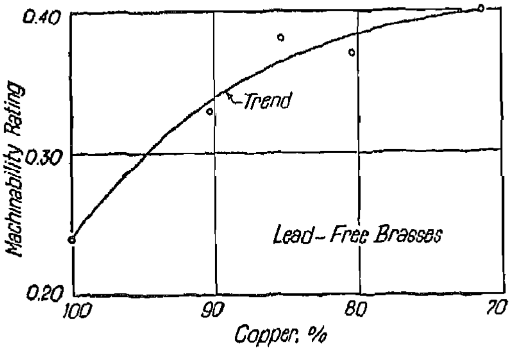

FIGURE 31-1. Effect of copper content on machinability rating of lead-free brasses as determined in a laboratory test. (*From Crampton*[3].)

Brass (Copper-Zinc). The addition of zinc to copper to form the simple brasses *results in a gradual and modest increase in machinability*, as is shown in Figure 31-1. For zinc contents up to 36 to 38 per cent the crystal structure of the brasses is fundamentally the same as for copper, face-centered cubic, differing only in the specific lattice constants, for these alpha brasses are solid solutions of zinc in copper. The changes in physical and mechanical properties are gradual and continuous as zinc increases and the machining characteristics vary accordingly. The nature of the chip is essentially constant from 0 to 35 per cent zinc.

Above approximately 38 per cent zinc, the beta phase begins to appear and the commercial alloys in this range are composed of a mixture of the alpha and beta phases, such as is shown in Figure 31-2. The beta phase is harder and more brittle than the alpha phase, and the mixed structure makes for improved machinability. Although chips are long for small amounts of beta, they become less tough with increasing beta content and are more readily handled.

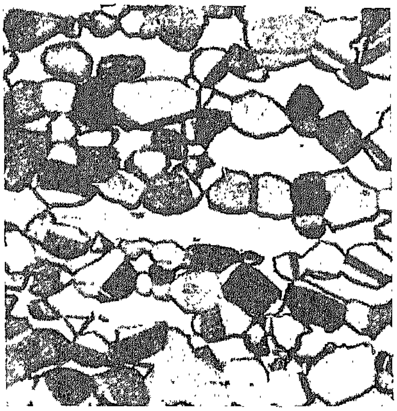

FIGURE 31-2. Typical microstructure of annealed lead-free alpha-beta brass, Muntz metal (60 copper, 40 zinc). Magnification 250X.

Small additions of tin and aluminum to brass to form the special brasses admiralty and aluminum brass (see Table 31-1) do not change the alpha microstructure, do increase strength and hardness, but have no significant effect on machinability. Likewise, the tin in naval brass makes no great change in the alpha-beta microstructure as compared with Muntz metal, nor is there any change in inherent machinability for equivalent structures.

Phosphor Bronze (Copper-Tin). The series of wrought tin or phosphor bronzes containing up to 10 per cent tin are all of the alpha type with crystal structure like that of copper. Although the alloys are distinctly harder and stronger than copper, and hence tend to resist tool penetration to a greater degree, they are in the same machining class with copper.

Cupro-nickel (Copper-Nickel). These alpha solid-solution alloys are also classed with copper for nickel contents up to at least 30 per cent, and are very tough. The free or precipitated particles of iron which may sometimes be present in the 10 per cent nickel alloy for iron contents of 1 to 2 per cent are apparently without effect on machining.

Nickel-Silver (Copper-Nickel-Zinc). The common alloys in this series containing from 10 to 18 per cent nickel and from 17 to 27 per cent zinc do not machine freely and have a machinability rating of 20.

Aluminum Bronze (Copper-Aluminum). Aluminum does not impart improved machinability to copper, and almost all of the commercial aluminum bronzes are found in the class of low machinability. The great hardness of the alloys containing 9 per cent or more of aluminum and additions of iron and other strengthening elements lead to further resistance to cutting.

An important exception in this class is an aluminum-silicon bronze containing about 7 per cent aluminum and 2 per cent silicon. Although one of the strong copper alloys, it machines readily, having a relative rating of 60. Its chips are of medium length and can be broken without great difficulty, a fact which may be associated with the properties of the phases found in its microstructure. In addition to the alpha phase, the beta phase and products of its decomposition are present, and, in contrast with other high-aluminum bronzes of fundamentally similar structures, the mixed structure leads to improved machinability to a greater extent even than in the alpha-plus-beta brasses (Muntz metal).

Silicon Bronze (*Copper-Silicon*). The group of wrought, alpha silicon bronzes containing about 1.5 and 3 per cent silicon as the essential alloying element behaves like the alpha copper-zinc series or simple brasses in that machinability is somewhat superior to that of copper. These alloys are classified among those of intermediate machinability.

Lead in Copper Alloys

Of the elements which may be added to copper and its alloys for the specific purpose of enhancing machinability, lead is the one most generally effective and commonly used. Having substantially no solid solubility in copper-base alloys, lead occurs as a dispersion of fine particles throughout the metal and is easily seen in the microstructure. The number of particles naturally increases with the percentage of lead in the alloys

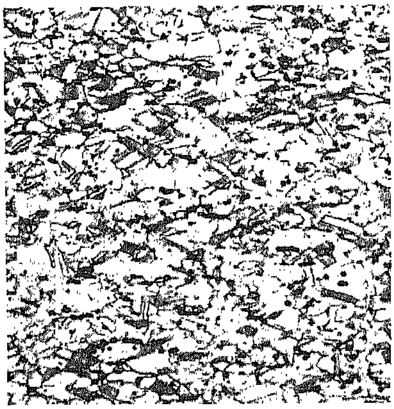

FIGURE 31-3. Typical microstructure of free-cutting brass (61.5 copper, 3 lead, 35.5 zinc), showing dispersion of lead particles. Magnification 75X.

and Figure 31-3 is typical of a free-cutting brass containing about 3¼ per cent lead.

The mechanism of the beneficial effect is not difficult to visualize. The cloud of soft lead particles constitutes a discontinuity of the metal structure, imparts no increment of hardness, and reduces the toughness, ductility, and malleability of the host alloy. Cutting tools therefore penetrate the leaded material with comparative ease and generate chips which are brittle and easily broken. The chips thus tend to be short and of favorable size for easy clearing away from the tools. In addition, the lead seems to provide a certain amount of lubrication between the alloy and the cutting tool.

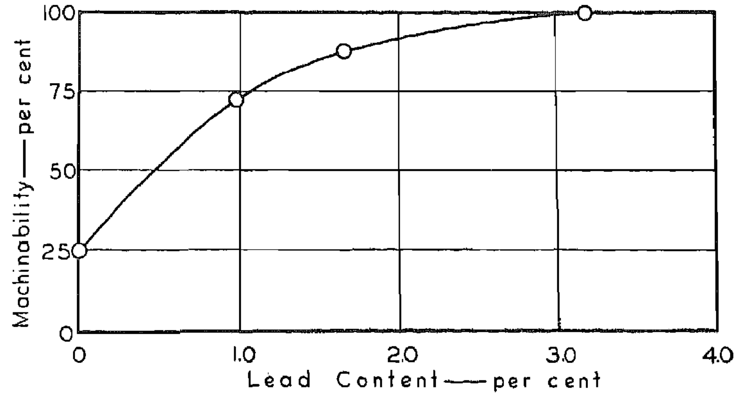

FIGURE 31-4. Effect of lead content on machinability of brass as determined in a laboratory test. (*From Crampton*[3].)

The effect of lead increases with concentration as is shown in Figure 31-4. In commercial brasses, the effect is first evident at about ¼ per cent in blanking operations, for such brass shears more cleanly and with less drag than does lead-free brass. Substantially maximum benefit with respect to machinability occurs at 3 to 4 per cent lead. This is fortuitous, for alloys of only slightly higher lead content are very difficult to produce in the wrought state due to deterioration of ductility and malleability. Free-cutting brass, containing approximately 61.5 per cent copper, 3 per cent lead, and 35.5 per cent zinc, has essentially the greatest machinability of all copper alloys and for this reason is used as the standard of comparison with a machinability rating of 100.

While extremely machinable, free-cutting brass will withstand only moderate bending and forming operations. When additional working operations are required, compromise in metal properties is offered by a series of leaded alloys wherein the lead content ranges downward according to the degree of other workability that is desired.

Tellurium and Selenium-containing Coppers

Elements other than lead may be added to copper to improve its machinability markedly. These are bismuth, sulfur, selenium, and tellurium. Tellurium copper has gained widespread commercial use both here and abroad and selenium copper has been used to some extent. Sulfur has not been used as an intentional addition to copper because its effect on machinability is less than that of tellurium or selenium. Bismuth is not used because of its disastrously embrittling effect on copper and copper alloys when present in only minute amounts.

Tellurium copper normally contains about 0.5 per cent of tellurium, which occurs in the copper as stringers of copper telluride compound as is shown in Figure 31-5. The separate particles of telluride reduce the ductility of the copper and serve to produce short chips after the manner of lead particles in leaded alloys. The machining characteristics of tellurium copper approach those of free-cutting brass. The advantages of tellurium copper over leaded copper are that it may be hot worked readily and is free from fire-cracking difficulties. In addition, there is less difficulty with respect to segregation and correspondingly more uniform machining characteristics.

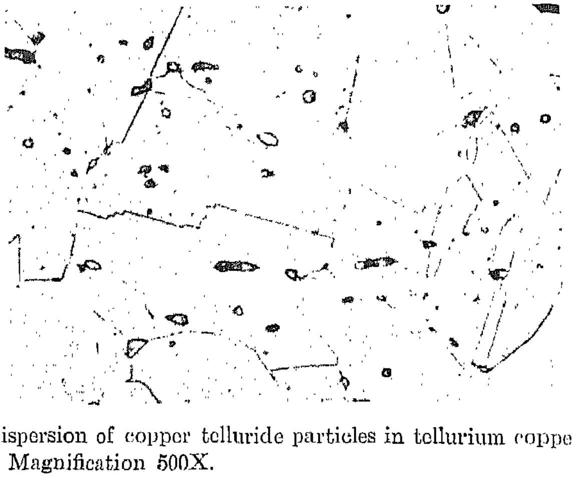

FIGURE 31-5. Dispersion of copper telluride particles in tellurium copper (99.5 copper, 0.5 tellurium). Magnification 500X.

The telluride particles appear to lack the lubricity of lead particles and a greater rate of wear of tools may be experienced when machining tellurium copper. For this reason, the use of carbide tools is often desirable for extended runs.

Approximately 0.5 per cent selenium is to be found in selenium copper, and the manner of its occurrence is similar to that of tellurium in copper, *namely, as discrete particles* of copper selenide, Cu_2Se.

Tellurium will also improve the machinability of other alloys of high copper content. In brasses, however, its effect decreases as zinc content increases and, for 35 to 40 per cent zinc, the beneficial effect on machinability is practically absent. This is in spite of the occurrence of the tellurium in a separate phase. Evidently the zinc alters the characteristics of this phase as compared with that in tellurium copper.

Effect of Temper on Machinability

Wrought copper and copper alloys which are to be machined are most often supplied in a cold-worked temper or are processed in other operations to such a condition. The cold work produces opposing trends with respect to machinability. On the one hand, the increased hardness and strength imparted by the cold work permit the work to stand up to the tool better than would material in a soft annealed temper, and the relatively greater increase in yield strength as compared with the increase in tensile strength due to the cold work provides a condition more favorable for separation of the chip from the work, according to some theorists. On the other hand, the increased hardness which accompanies the cold-worked temper produces greater resistance to penetration of the tool into the work. This has been demonstrated in certain laboratory tests and

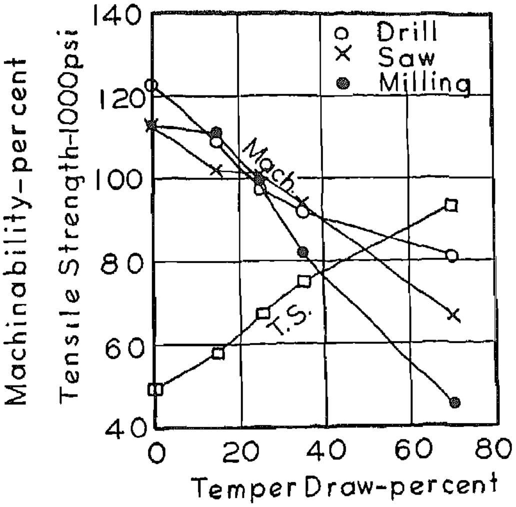

FIGURE 31-6. Effect of cold work on the machinability and strength of free-cutting brass as determined in laboratory tests. (*From Crampton*[3].)

TABLE 31-2. TURNING—TOOL ANGLES, SPEEDS, AND FEEDS

Alloy Group	Tool Material	Rake Angle, degrees		Clearance Angle, degrees		Surface Speed, feet per minute		Feed, inches per rev.	
		Back	Side	Side	Front	Roughing	Finishing	Roughing	Finishing
I	HS Steel	0	0—3	0—5	6	300—700	300—700	0.006—0.020	0.003—0.015
I	Carbide	0	2—6	4—6	4—6	400—800	500—1000	.015— .025	.005— .015
II	HS Steel	5—10	5—10	5—10	6—15	150—300	150—300	.015— .035	.005— .015
II	Carbide	0—5	4—8	4—8	4—8	300—500	400—600	.015— .030	.005— .015
III	HS Steel	10—20	20—30	10—20	10—15	75—150	75—150	.015— .040	.005— .020
III	Carbide	4—8	15—25	7—10	7—10	250—600	300—800	.015— .030	.008— .015

some typical results on the effect of cold work on machining free-cutting brass are given in Figure 31-6.

On the whole, a certain amount of cold work in the metal is desirable, and rod for machining work is usually finished with cold reductions up to 25 per cent. Even harder tempers, especially for small sizes, may be had if greater hardness and strength of product are desired.

Tools

High-speed tools are ordinarily used in machining copper alloys, although some economies may be obtained by the use of carbon steels for short runs. There is an increasing tendency toward the use of tungsten carbide, tantalum carbide, and stellite tools. These harder tools are particularly desirable for machining the more refractory alloys and those containing tellurium.

Tool Angles, Speed, and Feed

Cutting speeds and feeds may vary widely according to factors such as the alloy, its form and size, type of tool, size of machine, surface finish, and tolerances desired. The tool angles, speeds, and feeds listed in Table 31-2 for the turning operations are suggested for roughing and finishing cuts of approximately 0.045 to 0.125 inch and 0.015 to 0.030 inch in depth, respectively.

In Table 31-3, the conditions for milling are briefly outlined, while Table 31-4 lists values pertinent to drilling. Standard drills are made with both carbon steel and high-speed steel, while the slow-spiral and high-spiral drills, as well as drills of special design, such as flat and straight flute drills, are ordinarily of high-speed steel.

More comprehensive detailed data on tools, speeds, and feeds are to be found in several of the appended literature references, particularly in "The Metals Handbook[2]."

Coolants or Lubricants

Although some machining operations on copper alloys are performed dry, particularly for low-speed and low-production work, the use of coolants or lubricants is commonly desirable.

A light machine oil, sometimes called paraffin oil and having a viscosity of about 100 seconds Saybolt at 100°F, is a satisfactory lubricant for cutting, drilling, and tapping leaded or free-cutting copper alloys. One part of soluble oil to 10 to 20 parts of water may also be used.

More effective lubricants are required for copper and the copper alloys which are rated as difficult or moderately difficult to machine. For these materials, the use of any of the following is suggested:

(1) Mixtures of 75 to 90 per cent light machine oil and 10 to 25 per cent lard oil, with the amount of lard oil being increased as the difficulty of machining increases.

(2) Approximately 90 per cent light machine oil and 10 per cent highly sulfurized fatty oil (sulfur-base oil).

(3) Light machine oil with about 2 per cent tricresyl-phosphate.

Any of these lubricants may be removed by trichlorethylene in a vapor degreaser or by alkaline metal cleaners.

TABLE 31-3. MILLING (HIGH-SPEED STEEL CUTTERS)

Alloy Group	Rake Angle, degrees	Clearance Angle, degrees	Land, inches	Speed, feet per minute
I	0—10	10—15	0.015—0.030	200—250
II	0—10	6—12	0.015—0.030	150—200
III	0—15	5—15	0.015—0.030	50—150

TABLE 31-4. DRILLING (HIGH-SPEED STEEL DRILLS)

Alloy Group	Helix Angle		Rake Angle, degrees	Lip Clearance Angle, degrees	Point Angle, degrees	Speed,** feet per minute	Feed, inches per rev.
	Type	degrees					
I	Standard	26—30	0*	12—15	118	200—500	0.003—0.020
	Slow Spiral	10—22	0*	12—15	118	200—500	0.003—0.020
II	Standard	26—30	0*	12—15	118	75—250	0.003—0.020
	Slow Spiral	10—22	0*	12—15	118	75—250	0.003—0.020
III	Standard	26—30	Full	12—20	100—110	50—125	0.003—0.020
	High Spiral	40	Full	12—20	100—110	50—125	0.003—0.020

* Flatten cutting edge to prevent pulling into metal.

** Use approximately half speed with carbon-steel drills.

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Chapter 32

Welding, Brazing, Soldering, and Cladding of Copper and Its Alloys

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Copper and many of the copper alloys are readily joined by welding to produce strong homogeneous structures. Brazing has long been employed as a method of joining copper and its alloys; some of the alloys (Cu-Zn) are used as brazing filler metals. Soldering of copper and the alloys has long been a successful operation. Copper is employed as a metal to be clad upon other metals and itself may serve as the base upon which to clad other metals.

The term welding as currently defined by the American Welding Society encompasses eight major processes which include thirty-seven subsidiary processes. The eight processes are arc welding (including metal and carbon electrode), gas welding, brazing, resistance welding, induction welding, flow welding, forge welding, and thermit welding. Of this group the first five are the most commonly used in the welding of copper and its alloys; flow welding is used with certain copper-zinc compositions.

The successful performance of any welding operation requires the proper application of the principles of welding engineering, which have been summed up in the four headings: design, materials, workmanship, and inspection. These are not separate entities but interdependent factors, and due allowance must be made for the others in considering any one. Designing for welding must be in terms of the inherent capabilities of the processes and not merely adaptations of welding to other methods of fabrication. In addition to the usual details of physical form, dimensions, and mechanical strength, there is the added requirement of selecting the process which will produce the desired result in the most effective and economical manner. Closely related to these are the selection of the materials to fulfill the design requirements. This includes not only the metals to be welded (base metals), but also the filler metals used in the welding operation and welding fluxes if necessary. Workmanship is that phase of the over-all welding engineering problem that encompasses the preparation of the base metals for welding, the performance of the welding in a manner that will insure the results contemplated in the design, and the post-welding operations necessary to render the weldment suitable for its intended use. Inspection is the last step by means of which the product is checked for conformance to dimensional and design requirements as well as such codes or specifications as may be involved.

Copper and its alloys are available in a large number of analyses. However, for the purposes of this brief discussion only the significant types of general industrial importance can be covered. The principles herein covered are generally applicable to most of the alloys with only minor variations.

Copper

For the purposes of welding, copper must be considered in two classes, *i.e.*, those analyses containing oxygen and those without oxygen. The former includes electrolytic, Lake, fire-refined, and tough-pitch coppers; the latter includes deoxidized and oxygen-free coppers. Oxygen-bearing copper is not generally recommended for welded construction for the reason that a zone of the base metal is heated to a temperature at which all of the copper oxide is rejected to the grain boundaries, thereby creating a seriously weakened area. Some success has been reported in the welding of oxygen-bearing coppers by the use of welding processes which progress at fast speeds. The success of such techniques depends upon two factors: (1) at high welding speeds the time must be so short that virtually no oxide segregates; and (2) such minor segregation as does occur must not be sufficient to impair seriously the strength of the joint. Such welding processes are inert-gas metal-arc welding with consumable electrodes, and inert-gas tungsten-arc welding. Carbon-arc welding has also been used with varying degrees of success.

Deoxidized and oxygen-free coppers are readily joined by the arc and gas welding processes and brazing. However, because of the high thermal conductivity of copper it is necessary to employ high heat inputs for welding. It is also necessary to resort to preheating on heavy sections and large assemblies. Properly welded joints in oxygen-free copper will exhibit strength and ductility about equal to the annealed strength of the base metal. The properties of the weld may be improved by cold working.

Of all the welding processes available for welding copper, oxyacetylene, inert-gas tungsten-arc, inert-gas metal-arc, and carbon-arc welding are the most commonly used. In one respect oxyacetylene, tungsten, and carbon-arc welding are similar in that filler metal is introduced separately. Flux or an oxidizing flame adjustment is generally necessary with oxyacetylene welding; flux is necessary with carbon-arc welding; the use of inert gas in the inert-gas processes eliminates the necessity for flux. Welding rods* for all four processes must be free of oxygen, with the deoxidized types commonly available. Welding in the flat, horizontal, and vertical positions and to a limited extent in the overhead position may be performed by the oxyacetylene and inert-gas processes; carbon-arc welding is limited to the flat position.

For the oxyacetylene welding of copper the neutral oxyacetylene flame is recommended along with a suitable flux. Fluxes are of the type commonly employed for braze welding operations with copper-zinc (60-40) rods. Some authorities recommend the use of a slightly oxidizing flame and no flux. Due to the high conductivity of copper it is necessary to employ a tip one or two sizes larger than those normally used in steel welding. Additional heat for large masses is usually obtained by using one or more supplementary torches.

Inert-gas tungsten-arc welding of copper is best accomplished with direct current straight polarity (electrode negative), and helium; argon may also be used but will require higher currents. A silicon-deoxidized welding rod has been found to give the best results with this process. Heavy masses may require supplementary heating, as with an oxyacetylene torch.

Inert-gas metal-arc welding with consumable electrodes is performed with DC reversed polarity and argon or helium as the inert shielding gas. Filler metal is of the silicon-deoxidized copper analysis; silicon bronze and aluminum bronze may also be employed as filler metal, in which case the operation is one of braze welding.

Carbon-arc welding of deoxidized copper is performed with DC straight polarity (electrode negative) and either carbon or graphite electrodes. Silicon bronze filler metals, used with fluxes designed for this type of rod, are preferred, particularly when multiple-pass welds must be deposited. Phosphor bronze welding rods are also used (without flux), but should be limited to single-pass welds.

Copper (oxygen-bearing, deoxidized, and oxygen-free) is readily joined by torch, furnace, dip and twin carbon-arc brazing processes using either the copper-phosphorus or the silver alloy types of brazing filler metals. By proper selection of the brazing process and filler metal* it is possible to braze oxygen-bearing copper without loss of strength due to copper oxide segregation. However, prolonged heating above about 700°C (1300°F) is likely to cause oxide segregation and weak joints. The use of reducing atmospheres for furnace-brazing oxygen-bearing copper should be avoided, as this will result in "gassed copper," which is brittle. Torch brazing is performed with oxyacetylene, air-acetylene, or oxy-propane flames, or any combination of a fuel gas with oxygen or air that will produce the required temperature. A suitable brazing flux is necessary when using the silver alloy types of brazing filler metals; the copper-phosphorus alloys are "self-fluxing" on copper. Dip brazing, employing baths of molten brazing filler metal, is used for brazing copper wires. The high electrical conductivity of copper eliminates the use of the resistance and induction brazing processes. Flow and twin carbon-arc brazing are not used on copper.

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* Copper and copper alloy welding rods covered by ASTM-AWS Specification B259-52T (see reference 16).

All forms of copper are readily soldered with the common types of lead-tin solders—*in fact the classical soldering iron is usually a block* of copper. The particular composition of solder selected will depend upon (1) service conditions (*i.e.*, operating temperature), (2) working conditions, (3) economic considerations. Successful soldering is dependent upon proper cleaning (abrading), correct fluxing, and adequate heating. If all three features have been correctly handled the solder will flow readily and bond with the copper. Acid types of soldering fluxes are suitable on assemblies where it is possible to remove all flux residue after soldering. Any residue left on the work may lead to serious corrosion. For this reason, on electrical work, resin types of fluxes are generally used. Soldering copper is essentially a simple operation, as witness the success of the average layman with this operation.

Copper-Zinc Alloys

Copper-zinc alloys (both low and high brasses) may be welded by the carbon-arc, shielded metal-arc, inert-gas tungsten-arc, inert-gas metal-arc, gas, and flow welding processes; brazing is also used extensively. Resistance welding of the low brasses is difficult, whereas high brasses are more readily handled. The high zinc content of the high brasses creates some difficulty, particularly with the arc welding processes, due to the volatilization of the zinc. For this reason most of the filler metals for arc applications are not of the high-zinc compositions. Also this high evolution of zinc fumes necessitates the use of exhaust fans when welding these metals. Brasses containing lead in excess of 0.5 per cent are generally difficult to weld and sound joints difficult to produce.

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* Brazing filler metals covered by ASTM-AWS Specification B260-52T (see reference 17).

Carbon-arc welding of low brasses is best accomplished with the copper-silicon (3 per cent Si) rods and suitable flux. Copper-tin rods may be used for single-pass welds, but the copper-silicon rods should be used for multipass work. The high brasses may be carbon-arc welded with either a low-fuming brass (60 Cu-40 Zn) rod or the copper-silicon rod mentioned above. Preheating to 200°C (400°F) is essential to obtain fusion and sound weld metal. Flux for low-fuming brass rods is of different composition from that for the copper-silicon rods. Flux application is by means of paste (in alcohol) before preheating; additional dry flux may be added as welding progresses.

Shielded metal-arc welding of the brasses is performed with covered electrodes of either the grade A phosphor bronze composition or aluminum bronze (8 per cent Al, Classification ECuAl-A, in accordance with ASTM-AWS Specification B225-48T). Welding is performed with DC reversed polarity, although the aluminum bronze electrodes are also available for AC welding. The aluminum bronze electrodes provide deposits of higher strength and better corrosion resistance than do the phosphor bronze deposits. Phosphor bronze electrodes provide satisfactory strength up to about 40,000 psi. For optimum weldability with aluminum bronze electrodes use preheat and interpass temperatures of 200 to 260°C (400 to 500°F) on the low-zinc brasses; 260 to 370°C (500 to 700°F) for the higher brasses. Phosphor bronze electrodes may be used with lower values of preheat.

Inert-gas tungsten-arc welding of the copper-zinc alloys is complicated by the evolution of zinc oxide fumes, which interfere with the action of the arc. High welding speeds will tend to minimize this trouble, hence machine welding is preferred. Welding may be performed with either DC or AC. With DC either helium or argon may be used; with AC use argon. Welding with AC and argon appears to provide the best control of oxide fumes. Copper-silicon (3 per cent Si) welding rods have produced the best results with this process.

Inert-gas metal-arc welding with consumable electrode filler wire has proved satisfactory in the welding of manganese bronze castings of the type employed for ship's propellers. Welding is performed with DC reversed polarity (electrode positive) and argon as the shielding gas. Filler wire is of the 8 per cent aluminum bronze analysis. Filler wires with high zinc content are unsuitable for this process; even as little as 0.5 per cent Zn can contribute to arc instability and poor results.

Gas welding is extensively used on the copper-zinc alloys with excellent results. For welding the low brasses, since there are no rods of matching analysis available, it is common practice to use copper-silicon (1½ per cent Si) rods. The conventional brass (60 Cu-40 Zn) braze welding rods may also be used if corrosion conditions are not severe. For welding the high brasses the conventional brass rods (sometimes called bronze) are of substantially the same composition as the base metal and are therefore used. These same rods are extensively used for brazing of steel, cast iron, malleable iron, copper, etc., and dissimilar combinations of these metals. The use of proper fluxes is of the greatest importance in this work. Fluxes suitable for use with the copper-silicon rods are not satisfactory with the copper-zinc rods. Because of the high zinc content the flux must not only perform the usual cleaning functions but must also suppress or control the volatilization of the zinc. Generally a neutral oxyacetylene flame is used for welding these metals.

Flow welding, sometimes referred to as "burning in," is used extensively for welding on large sections of cast manganese bronze ship propellers and is accomplished by flowing molten metal over the joint until fusion occurs. In the performance of flow welding the parts are aligned and held in position by tack welding with the arc or other convenient means. The area along the joint is provided with lateral dams and positioned so that gravity will assist the flow of the metal. The assembly is preheated, following which molten brass of the same composition as the parts is poured over the joint. The first passage of molten metal serves to raise the temperature of the parts and when fusion temperature is reached the weld is made between the parts and the molten filler metal.

The copper-zinc alloys are readily brazed with the silver and copper-phosphorus alloys; brass brazing filler metals may be used providing there is sufficient difference in the melting points. Flux suitable for the brazing alloy employed should be used, although the copper-phosphorus alloys may be substantially self-fluxing if the copper content of the base metals is high. Lead, when present over about 0.50 per cent, may prove troublesome and requires liberal applications of flux.

Because of their low electrical resistance, low-zinc brasses are resistance welded with difficulty. Low electrode pressure and high energy input are necessary. Electrode sticking and low strengths will be encountered with these analyses. High-zinc brasses are resistance welded with good results over a wide range of conditions. Energy input should be toward the high side and electrode forces should be above 400 pounds. Long welding times should be avoided, as this contributes to the weld "blowing through."

The brasses are extensively joined by soldering, notwithstanding the fact that tin and zinc do not react well together. If the brass is tarnished, cleaning must be by abrading or acid pickling. The "acid" or chloride type of fluxes yield best results on brasses. Solder containing 60 per cent Sn is preferred but 50 per cent Sn may be used. Antimony, due to its strong affinity for zinc, must not be present in soldering. The acceptable limit is 0.25 to 0.50 per cent Sb.

Copper-Silicon Alloys

Copper-silicon alloys may be successfully welded with the carbon-arc, shielded metal-arc, inert-gas tungsten-arc, inert-gas metal-arc with consumable electrodes, submerged arc, gas, and resistance welding processes. These alloys are also brazed with excellent results.

Carbon-arc welding of the silicon bronzes is performed with rods of the same analysis and suitable flux. Welding proceeds readily because of the relatively low thermal conductivity of this metal; oxides are not particularly troublesome. Graphite electrodes are preferred to ordinary carbon electrodes. Phosphor bronzes (8 per cent Sn, Grade C or 10 per cent Sn, Grade D) may also be used as filler metal for single-pass welds not exceeding ¼ inch.

Shielded metal-arc welding of the silicon bronzes is readily accomplished with either silicon bronze or aluminum bronze electrodes. Since the metal is hot short, overheating must be avoided and interpass temperatures should be maintained below 65°C (150°F); preheating and postheating must be avoided. Welding in the flat position is preferred, but the silicon bronze electrodes may be used in the vertical and overhead positions.

Inert-gas tungsten-arc welding of the silicon bronze alloys is performed with DC straight polarity (electrode negative) and either helium or argon; helium is preferred because of the higher arc energy. Filler metal matches the base-metal analysis, although aluminum bronze may be used. Since welding progresses at relatively fast speeds, hot-short cracking is not as serious as with slower welding processes.

Inert-gas metal-arc welding with consumable filler metal is very successfully employed in the welding of silicon bronze. Either helium or argon with DC reversed polarity (electrode positive) may be used. Filler wire is usually of the same composition as the base metal. Welding speeds are higher than those with the tungsten arc, hence hot-short cracking is even less.

The silicon bronzes are successfully welded by the submerged-arc process, using fluxes designed for this alloy. Filler metal is of the same composition as the base metal.

Oxyacetylene welding of the silicon bronzes is performed with either a neutral flame or a slightly oxidizing flame and flux. Welding rods are of the same analysis and the flux should be one suitable for use therewith. Braze welding with copper-zinc rods and suitable flux may also be employed. It is desirable to maintain a small weld pool to insure rapid cooling of the metal to avoid hot-short cracking. The use of the oxidizing flame assists in the maintenance of the small pool.

The silicon bronzes are about the best of the copper alloys for resistance welding. A wide range of conditions may be employed and secure good results.

Brazing by any of the conventional brazing processes may be performed on the silicon bronzes. Adequate flux protection must be provided to avoid formation of refractory silicon oxide. The base metal should preferably be in the annealed condition, since this composition is subject to intergranular penetration, if under even relatively low stresses, and this may lead to cracking.

Soldering of silicon bronzes presents a problem in that the presence of silicon oxide renders the tinning by the solder difficult. Mechanical abrading is satisfactory provided soldering is performed quickly enough to prevent re-formation of the oxide. Otherwise it is necessary to employ a very active flux.

Copper-Tin Alloys (Phosphor Bronzes)

The phosphor bronzes are best joined by the shielded metal-arc, inert-gas metal-arc, and resistance welding processes, and brazing. Inert-gas arc, submerged-arc, and gas welding processes are sometimes used, but are subject to limitations. Carbon-arc welding is not generally used. Since these alloys exhibit a pronounced tendency to hot shortness, it is important that they be welded as rapidly as possible; this factor limits the use of certain welding processes. Lead, if present over about 0.50 per cent, can be troublesome in welding.

For the shielded metal-arc welding of the phosphor bronzes, two electrode compositions are available, *viz.*, type A and type C (classifications ECuSn-A and ECuSn-C in accordance with ASTM-AWS Tentative Specification B225-48T). Preheat and interpass temperatures of 150 to 200°C (300 to 400°F) should be maintained. Fast welding with small (stringer) beads should be employed. Hot peening improves tensile strength and ductility.

The inert-gas metal-arc welding of copper-tin alloys produces satisfactory results using filler metal wire of either the A or C grades. One further application is that of leaded phosphor bronze—a doubtful operation by any other process. In this instance the leaded phosphor bronze is overlaid on steel for steel-mill guides.

The copper-tin alloys lend themselves quite well to resistance welding, since their electrical conductivity is low. The range of operating conditions is quite wide and energy levels are low. Some cracking may be encountered due to the hot-short characteristics of these alloys.

Brazing of the phosphor bronzes is readily performed with the copper-phosphorus, silver, and brass brazing filler metals (if the melting points of base metal and filler metal differ sufficiently). Suitable brazing flux is, of course, necessary.

Inert-gas tungsten-arc welding is used for these alloys, employing either helium or argon and matching filler metal. Most experience to date seems to indicate that a small amount of porosity may be expected. There are few data on the submerged-arc welding of copper-tin alloys, although some success has been reported in welding those with lower tin contents. Gas welding is limited to the ASTM grade E (1.0-1.5 per cent Sn) and the grade C (8 per cent Sn) alloys. A flux, of the type used in braze welding with copper-zinc rods, is commonly used. The spreading heat characteristic of the oxyacetylene process is not compatible with the hot-short nature of these alloys and in consequence is seldom used.

The soldering of the copper-phosphorus alloys is accomplished with about the same ease as experienced in soldering copper. Cleaning, fluxing, etc., are, of course, necessary.

Copper-Aluminum Alloys (Aluminum Bronze)

The aluminum bronzes are readily welded by the carbon-arc, shielded metal-arc, inert-gas tungsten-arc, inert-gas metal-arc, and submerged-arc processes. Brazing is satisfactorily performed on these alloys. While resistance welding is used, some difficulties may be anticipated. Gas welding is not used.

Shielded metal-arc welding of the copper-aluminum alloys is readily performed, since these alloys do not exhibit hot shortness. Five classifications of covered electrodes are available, *viz.*, ECuAl-A, ECuAl-B, ECuAl-C, ECuAl-D, and ECuAl-E (AWS-ASTM Tentative Specification B225-48T). The A and B grades are used for joining aluminum bronze base metals of equivalent compositions and also braze welding of steel, cast iron, etc., and dissimilar metals. The C, D, and E grades are used for joining similar analyses of base metals and for overlaying bearing and wearing surfaces. For grades A and B the preheat and interpass temperature should be 200°C (400°F); for the harder grades temperatures in the vicinity of 370 to 425°C (700 to 800°F) are needed to prevent cracking.

Aluminum bronzes are successfully welded with the inert-gas tungsten-arc method using either helium or argon. For the welding power source either DC or AC may be employed. With AC either the balanced AC type (high open-circuit voltage) or continuous high frequency may be used; with continuous high frequency use only argon. The filler metal matches base-metal analysis.

Inert-gas metal-arc welding with consumable electrodes (in coil form) has proven to be eminently satisfactory for the welding of the copper-aluminum alloys; in fact, it is the only method by which welding vertically and overhead can be accomplished with these compositions. Welding power is DC reversed polarity (electrode positive). The shielding gas may be either helium or argon. The former gives sounder welds but with some spatter; the latter gives bright smooth-surface welds but with some internal porosity. Mixing these gases seems to effect results that are better than those provided by either gas alone. Preheat and interpass temperatures of 150 to 200°C (300 to 400°F) are requisite to assure better results.

Submerged-arc welding of the aluminum bronzes is satisfactorily performed using appropriate flux. Filler wire matches base-metal composition.

Resistance welding of these alloys is difficult to perform because of troubles encountered with electrode sticking and pick-up. Strength will be only moderately high. Difficulties may be minimized by avoidance of long welding times, high currents, and pressures.

The copper-aluminum alloys present special difficulties for brazing due to the formation of aluminum oxides. Special brazing fluxes are necessary to overcome this condition. The standard silver brazing alloys may be used. If dissimilar metals are to be brazed, then the fluxes used must be compatible with the metals involved. This may require the use of two fluxes, since the one for aluminum bronze may not work with other metals.

Soldering of the aluminum bronzes is also complicated by the presence of the aluminum oxide. This necessitates the use of a strongly active flux. One flux recommended employs equal parts of HCl and $ZnCl_2$ (25 per cent in water). Assemblies must be well washed after soldering.

Copper-Nickel Alloys

The copper-nickel alloys are welded by the shielded metal-arc, inert-gas tungsten-arc, inert-gas metal-arc, submerged-arc, and gas welding processes; brazing is also used.

Shielded metal-arc welding of copper-nickel alloys (nominally 30 per cent Ni-70 per cent Cu with Ni in a range of 20 to 30 per cent) is performed with covered metal-arc electrodes and DC reversed polarity. The electrodes are of the nominal composition and conform to classification ECuNi (AWS-ASTM Tentative Specification B225-48T). Since these alloys are hot short, no preheating should be used and interpass temperature should be held below 65°C (150°F). Peening improves mechanical properties.

The copper-nickel alloys may be welded with the inert-gas tungsten-arc process, using either DC or AC; the latter may be either the balanced type or continuous high frequency. Shielding gas may be either helium or argon; use only argon with high-frequency stabilized welders. Filler metal is of the same analysis as the base metal.

The inert-gas metal-arc welding process may be used for welding the copper-nickel alloys, employing DC reversed polarity and helium or argon. Filler metal wire should be of the same composition as the base metal.

The copper-nickel alloy 70 Cu-30 Ni has been welded by the submerged-arc process in the fabrication of heat exchangers for marine service.

Gas welding of the copper-nickel alloy is accomplished in about the same manner as welding of monel. The flame should be adjusted with a slight excess of acetylene. A flux suitable for welding is necessary in welding this alloy. Rods must be of the same composition with additions of Mn or Si as deoxidizers. The welding speed should be rapid and welds once started should be completed without stopping. Base metal should be melted as little as possible and manipulation of the base metal should be avoided.

The copper-nickel alloys may be brazed successfully using the silver-alloy brazing filler metals; phosphorus-containing alloys should be avoided. Since these alloys are subject to intergranular corrosion, it is desirable to use them in the stress-relieved condition for brazed assemblies. Apply brazing flux liberally to reduce formation of nickel oxide.

Soft soldering of the copper-nickel alloys is best accomplished with the acid types of fluxes; flux residue must, of course, be removed after soldering. Standard types of solders, suitable for the service conditions, may be used.

Copper-Beryllium Alloys

The copper-beryllium alloys are frequently used in a heat-treated condition and welding or brazing may alter the heat-treated properties. Therefore it is recommended that heat-treating operations be performed after welding. Welding of these alloys may be performed with the carbon, shielded metal-arc, and inert-gas tungsten-arc welding processes. Brazing is also a suitable joining process. Data are insufficient to make any statements with respect to the suitability of the other processes. Copper-beryllium alloys may be soft soldered.

Carbon-arc welding is used to join weldments of beryllium copper as well as applying overlays of this metal on other metals. Filler metals are the same as the base metal or are provided with additions of nickel to improve mechanical properties in the heat-treated condition. Filler metal must be flux-coated and for this purpose either the standard metal-arc electrodes or specially coated rods, 36 inches long, may be used. Preheat and interpass temperatures should be in the range of 315 to 370°C (600 to 700°F).

Shielded metal-arc welding of the copper-beryllium alloys is performed with DC reversed polarity (electrode positive) and covered electrodes. The nominal composition of the core wire of these electrodes is 1.1 per cent Ni and 2.50 Be. Aluminum bronze electrodes may also be used where the presence of this dissimilar metal is not objectionable. On large weldments preheat and interpass temperatures in the range of 315 to 370°C (600 to 700°F) will prove helpful.

Inert-gas tungsten-arc welding may be used on beryllium copper and because of the inert gas, flux is not necessary. Welding current may be either DC straight polarity (electrode negative) or AC. With AC either the high open-circuit voltage type or continuous high frequency with standard welding transformers may be employed. Shielding gas may be helium or argon; with AC and continuous high frequency use only argon. Bare filler metal is the same analysis as the base metal. Welding procedures are similar to those employed with the aluminum bronzes.

Brazing of the copper-beryllium alloys may be accomplished provided that the joint areas are thoroughly cleaned to remove the refractory beryllium oxide. Special brazing fluxes are necessary, usually high in fluorides, to handle the oxide. If it is necessary to braze assemblies for subsequent heat treatment, then the brazing filler metal should have a brazing temperature range above the heat-treating temperature, *i.e.*, 775°C (1425°F). When brazing previously heat-treated parts, the brazing temperature range should be low and the brazing operation should be accomplished quickly.

Soft soldering on beryllium copper is complicated by the presence of the beryllium oxide. While shot-blasting or grinding offer some relief to this problem, it is difficult to prevent the re-forming of the oxide. Special, highly corrosive, fluxes should be used where the residue can be completely removed. Electrotinning is sometimes helpful in this connection.

Dissimilar Metals

The joining of dissimilar metals by any of the welding processes is dependent upon the relative melting points of the metals, the type of connection necessary, and the service conditions. The joining of metals within the group of copper and copper alloys is perhaps simpler than combinations with other metals such as iron, steel, nickel, etc. If the metals to be joined have melting points close to each other (*e.g.*, the copper-zinc alloys), it is often possible to weld the combination with a filler metal which matches one or the other. It has been suggested that if the melting points are within 50°F, the operation may be considered one of welding. When the melting points differ widely it becomes necessary to resort to braze welding or brazing, since these processes depend not upon melting of the base metals but rather on a surface phenomenon for their bond strength. Braze welding by the arc-welding techniques usually employs filler metals of the aluminum bronze or silicon bronze analyses. In gas-welding techniques the copper-zinc filler metals are commonly used. For brazing, the several types of brazing filler metal may be used, subject to their limitations. Soft soldering is, of course, another solution to this problem of joining dissimilar metals. Where fluxes are used it may be necessary to resort to more than one type of flux in order to accommodate the different base metals.

CLAD METALS

Copper may be clad on other metals or copper may be clad with other metals, in each instance to achieve some special purpose. Copper is provided as a cladding on steel to reduce the over-all cost of the composite or to increase the strength while maintaining high conductivity in the copper cladding. Copper is also clad on aluminum for the purpose of combining the lightness of aluminum with the conductivity of copper. Copper is clad with certain silver brazing alloys in order to facilitate the brazing of certain types of tools and improve their performance.

The method of joining the copper to other base metals is often considered a trade secret. However, certain methods are fairly well known, and these are plating, brazing, hot rolling of layers of copper and steel in specially prepared "sandwiches," and pouring the molten metal (of lower melting point) around ingot or bars of the higher melting metal.

The production of copper-clad sheet and plate in thicknesses ranging from $\frac{3}{16}$ to $1\frac{1}{4}$ inches is one of the more extensive applications. This composite material is produced with claddings of oxygen-free high-conductivity or phosphorus-deoxidized copper on steel plate. A plate of the specified copper material is placed on a steel slab, then a similarly prepared assembly of steel and copper material is placed on top of the first one with an infusible parting compound between them. The steel backing plates are made slightly longer and wider than the cladding plate so that, after the four-layer pack or "sandwich" is formed, there is a groove running around the four sides of the assembly. Steel bars are used to fill in this space and act as backing bars for a weld which runs completely around the perimeter of the assembly.

This weld completely seals the pack, and prevents contamination of the copper and also movement of the components during subsequent heating and rolling.

The composite pack is heated in a soaking pit to the required temperature and rolled on a mill. The heavy rolling pressure on the composite material reduces its thickness uniformly and permanently bonds the copper to the steel. The relative proportions of copper to steel as established in the original assembly are preserved in the rolled composite plates. After rolling, the pack is sheared or oxygen-cut inside the weld edge as close to the edge of the cladding as possible. The pack is then separated into two copper-clad plates, each of which consists of a steel backing with a layer of the cladding metal permanently bonded to one surface.

The production of copper-clad steel for wire, pole-line hardware, and fencing is another typical example. In this instance accurately prepared billets are specially cleaned and placed in molds. The mold and its steel core is next heated in a furnace to such a temperature that when the molten copper is poured around the steel a weld between the two metals is made. Actually this "weld" is more in the nature of a braze weld. Subsequently this composite ingot is processed to produce the rods, wire, etc., that may be required.

Copper and its alloys may serve as the base upon which other metal or alloys are clad for special purposes. The principal application of this cladding is in the field of machine tools, where copper-cladding on one or both sides is used for the production of carbide-tipped tools. The cladding material is the silver brazing alloy containing silver-copper-cadmium, zinc, and nickel; it is used especially because of its ability to "wet" carbide tips. The presence of the copper (or sometimes copper alloys) is for the purpose of absorbing the service shocks to which such a tool is subjected.

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Chapter 33

Production and Use of Copper

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World production of primary copper in the last fifteen years has varied from a low of about 2,000,000 short tons in 1946 to about 3,000,000 tons in the maximum war-production year of 1943. During this period production in the United States has been roughly one-third of the world total and the combined United States, Canadian, and South American production has amounted to roughly two-thirds of the total.

Inasmuch as consumption of copper in the United States prior to the 1930's was somewhat less than production, usually small to considerable quantities of copper were exported. During and since the war this country has accounted for slightly less than one-third of the primary copper production of the world but has consumed roughly half of it; thus during this time it has become a large importer of copper.

According to studies recently published by the National Industrial Conference Board, the growth trend for consumption of primary copper in the United States starting in 1885 shows a sharply increasing initial rate which becomes progressively less over the period covered. In 1932, which is indicated as the "critical year," the consumption trend was increasing at the rate of more than 2.7 per cent annually. At present the increase in consumption is at the rate of 1.7 per cent per year. This trend graph, of course, smooths out marked variations which may come in any one year. For instance, consumption in 1950 was about 29 per cent above this trend line. By comparison, in the steel industry the "critical year" was given as 1917, at which time the rate of growth was 4.03 per cent, tapering off to 1.04 per cent in 1950.

Consumption of primary copper per capita in the United States has varied markedly over a long time. In the high prosperity period of the late 1920's this ranged from about 15 to 19 pounds per person, but fell off in the depression period of the early 1930's to as low as 5.5 pounds per person. During the war years consumption ran as high as 22 or more pounds per person, although such a figure has no very great significance so far as any normal period is concerned. In the postwar period this figure has been reasonably constant at about 16 to 18 pounds per capita.

Accurate and reliable data on consumption of copper for various specific end uses are surprisingly difficult to obtain. Up through the year 1940 the American Bureau of Metal Statistics published annually a breakdown of use of copper by the major consuming industries, but discontinued this presentation the following year. Their data for 1940 are reproduced in the left-hand columns of Table 33-1. The figures include the copper contained in alloys as well as that used in the form of the pure metal. For convenience, in addition to tonnages, there are also included figures for the percentage of the total consumption represented by each field of use.

In the right-hand columns of Table 33-1 there are reproduced figures pertaining to these same consuming industries compiled in 1950 by the Copper & Brass Research Association, using the best sources of information then available. A comparison of the 1940 and 1950 data in this table is very interesting. Even though total consumption increased some 30 per cent, it is surprising to see how little change there is in the consumption in most fields on the basis of percentage of the total use. None of the larger consuming industries shows a significant change in percentage of the total, although the proportionate increase in the fields of railroads, refrigerators, shipbuilding, and air conditioning are worthy of note. The fact that figures are given in 1940 for castings but not in 1950 is not to be taken to mean that there was no consumption in this field in 1950, but rather that this tonnage has been absorbed statistically in other categories.

TABLE 33-1. CONSUMPTION OF COPPER BY INDUSTRIES

1940 Figures from American Bureau of Metal Statistics
1950 Figures from Copper & Brass Research Association

Industry	1940 Short Tons	1940 Per Cent	1950 Short Tons	1950 Per Cent
Electrical	247,000	23.1	303,000	21.7
Telephone and telegraph	49,000	4.6	87,000	6.2
Light and power	74,000	6.9	100,000	7.1
Wire cloth	9,200	0.9	10,000	0.7
Other rod and wire	120,000	11.2	127,000	9.1
Ammunition	26,000	2.4	70,000	5.0
Automobiles and trucks	103,000	9.6	145,000	10.3
Building	102,000	9.5	135,000	9.7
Clocks and watches	4,400	0.4	7,000	0.5
Copper-bearing steel	4,700	0.4	8,000	0.6
Radiators and heating	2,900	0.3	9,000	0.6

TABLE 33-1. CONSUMPTION OF COPPER BY INDUSTRIES (*Continued*)

Industry	1940 Short Tons	1940 Per Cent	1950 Short Tons	1950 Per Cent
Castings	35,000	3.3	....	.....
Radio and television	32,000	3.0	50,000	3.6
Railroads	5,700	0.5	25,000	1.8
Refrigerators	10,500	1.0	26,000	1.8
Shipbuilding	8,700	0.8	22,000	1.6
Air conditioning	6,000	0.6	30,000	2.1
Others	81,500	7.6	95,000	6.8
Manufactured for export*	148,400	13.9	151,000	10.8
TOTAL	1,070,000	100.0	1,400,000	100.0

* Comprises the copper content of all mill products and all fabricated products which were exported, but does not include any raw copper exported as such.

Early in 1952 a new breakdown of copper consumption was made and it is believed that these figures more accurately reflect present consumption than any other now available. These are reproduced in Table 33-2. Particular attention is called to the fact that in the table the *electrical* components of all of the other six major market classifications are included with the first item; *i.e.*, as electrical. Among the market classifications included are not only the first three classifications of Table 33-1, electrical, telephone and telegraph, and light and power, but also such applications as radio and television, refrigeration, air conditioning, electric clocks, electrical wiring in building, etc., which appeared separately in Table 33-1. Likewise metal used in the form of bolts, nuts, rivets, screw machine products, etc. has been apportioned to consuming markets, as has the tonnage moving through jobbers, dealers, and distributors. Thus it is not possible to make a direct comparison between Table 33-1 and Table 33-2.

TABLE 33-2. 1946-1950 ESTIMATED REFINED COPPER USAGE BY INDUSTRIES

	Per Cent
Electrical, including power and light companies, communications, and manufacturers of all types of electrically motivated equipment	55
Construction, including contractors' products	15
Automotive	12
Machinery, industrial equipment, and tools	9
Domestic, commercial, professional, and scientific equipment	4
Ammunition, sporting goods, and miscellaneous	3
Transportation other than automotive—rail, water, and air	2
	100

Some further light on end use is shown by figures of refined copper produced according to shapes. While this varies somewhat from year to year, a rough breakdown for recent years indicates the following approximate percentages:

	Per Cent
Wirebars	60
Ingot and ingot bars	7
Cakes	15
Cathodes	6
Billets	12
	100

It must be remembered that the above figures are for primary refined copper only and do not take into account any secondary metal. Obviously, wirebars ultimately result in production of high-conductivity wire (and a small percentage of bar), mostly used for electrical current-carrying purposes. The cakes are invariably finished into sheet and strip, a very large proportion of which goes into building construction, including roofing, leaders and gutters, etc. Practically all of the billets are used for production of seamless copper tube, much of it in such important products as copper water-tube and refrigerator tube. The ingots, ingot bars, and cathodes are substantially all used for melting and alloying, which field also accounts for most of the consumption of scrap. Incidentally, with regard to primary and secondary metal, it is interesting to compare copper with the three other most important nonferrous metals. Table 33-3 gives very approximately the situation for the available supply over the years 1947 to 1949 inclusive.

TABLE 33-3. APPROXIMATE BREAKDOWN OF CONSUMPTION OF SOME NONFERROUS METALS

	Primary		Secondary	
	Domestic[1]	Imported	New[2]	Old
Copper	40	20	20	20
Lead	30	30	7	33
Zinc	50	35	11	4
Aluminum	60	15	20	5

[1] Includes production from imported ores such as bauxite in the case of aluminum.
[2] Scrap from fabricators (*not* mill scrap).

TYPES OF ALLOYS AND PROPERTIES DETERMINING THE FIELD OF USE

Many variations of commercial coppers are available, with differences ranging from slight to important resulting either from the method of production or from intentional minor additions of other metals, eighteen such being recognized by the American Society for Testing Materials in its Classification of Coppers B-224. For most practical purposes, however, the average user need only know that there are two basic varieties determined by the refining process, and three major types as regards chemical composition. Well over 85 per cent of all copper is electrolytically refined. Essentially, furnace-refined or as it is sometimes called fire-refined, copper differs from electrolytic simply in the elimination of the step of electrolytic purification. Since electrolytic refining is more costly than the simple furnace refining, it is used only where either one or both of two conditions exist: either the original ore contains such quantities of certain undesirable impurities as to necessitate electrolytic refining for their complete removal, or else it contains sufficient amounts of silver and gold, recoverable in electrolytic refining, to more than pay the cost of that operation and thus leave a profit.

Regardless of how refined, the three major types as determined by composition are tough-pitch, phosphorized, and oxygen-free coppers, which have been discussed in other chapters of this book. By far the largest amount of copper fabricated in the form of wire, sheet, or strip is tough-pitch copper, which is well suited to most applications.

In wrought alloys the brasses account for a very large proportion of total production. One major group comprises the plain or nonleaded brasses, which cover the range from about 60 per cent copper-40 per cent zinc to about 95 per cent copper-5 per cent zinc. As a group, these alloys combine to a very unusual degree good strength, excellent ductility and malleability, high atmospheric and aqueous corrosion resistance, and attractive color. The latter ranges from copper-red through reddish gold to the yellow of 70-30 brasses, and large volumes of material are selected for specific applications because of distinctive color in preference to other materials which might serve equally well in other respects.

Another major group covers the leaded brasses, in which lead in amounts up to approximately 3 per cent is added to copper-zinc alloys solely to improve machinability, the effect on this property being quite profound. Wherever extensive machining of any wrought brass is necessary and where the concomitant reduction in ductility and workability can be tolerated, leaded brasses invariably are used in preference to the plain ones.

There is also a considerable group of special brasses where small quantities of such elements as aluminum, tin, iron, manganese, etc., are added to give improved strength, hardness, wear resistance or corrosion resistance, or some combination of these. Thus, for example, admiralty brass, which contains approximately 70 per cent copper-29 per cent zinc-1 per cent tin, with or without a small amount of dezincification inhibitor, has been used for years as a highly corrosion-resistant heat-exchanger tube alloy.

The phosphor bronzes, more properly called tin bronzes, are copper-base alloys with tin varying from approximately 1 to 10 per cent, deoxidized with phosphorus in amounts up to perhaps 0.25 per cent. These alloys as a group being harder, stronger, and more resilient than the brasses, are highly favored for making springs of all types which must be corrosion-resistant, nonmagnetic, and mechanically stable.

The nickel silvers, which are copper-nickel-zinc alloys containing from 5 to 25 per cent nickel, are used not alone because of the very attractive white color but also where very high corrosion resistance is necessary. They find wide use in low-cost flat or tableware or as a base for silver-plated tableware and hollowware.

The cupro-nickels, containing usually from 10 to 30 per cent nickel and the balance copper, are as a class the most corrosion-resistant of the wrought copper-base alloys. The 70-30 alloy has for years been the one favored for condenser tubes on naval and other vessels where maximum resistance to corrosion by salt or polluted waters is essential. More recently, the 10 per cent nickel alloy with small additions of iron and manganese has been found to have corrosion-resisting properties approaching those of the 70-30 alloy.

The silicon bronzes containing from about 1 to 3 per cent silicon with or without third elements are as a group useful because of high strength, high corrosion resistance, and excellent workability. They are much used for fabricating tanks, bolts, fasteners, etc., or wherever their capacity for being joined by most welding procedures is important.

There are also many other special and engineering alloys, including age-hardening alloys, which cannot be mentioned in detail in a general chapter of this kind. Most of the producing mills have one or more such alloys which have been tailored to meet some special set of use conditions, usually a combination of properties not ordinarily shown to a desirably high degree by any of the more common alloy groups above discussed.

In the field of castings, the alloys comprising by far the largest use are the copper-tin-lead alloys, sometimes also containing small amounts of zinc. In this group the tin content ranges from about 5 to about 10 per cent, lead from about 5 to about 25 per cent, and zinc when present from about 1 to about 5 per cent. All have a generally copper-reddish color; all are adapted to making clean, sound castings suitable for a wide variety of uses, including pressure castings. Generally speaking, the cost will increase with increasing copper and especially with increasing tin content. Strength and hardness vary more or less directly with increasing tin content but inversely with copper content. All are more readily machinable due to the lead present, but that element also has an important role in bearings where it permits "wearing-in" and minimizes seizing and galling when lubrication is not adequate.

There is also considerable production of the so-called manganese bronzes which are in reality low copper-content brasses containing about 1 per cent, more or less, of the elements iron, aluminum, and manganese, and sometimes also tin and lead. These alloys are yellow in color, of relatively high strength, and are used for structural purposes but generally are not suitable for bearings.

There is also a group of aluminum bronzes or copper-base alloys containing usually from about 9 to 11 per cent aluminum and perhaps 1 to 4 per cent iron; these are quite strong, hard, and corrosion-resistant, and are used primarily for such things as structural members, gears, marine propellers, and for uses requiring good strength at moderately elevated temperatures.

This brief review of the characteristics of the several types of both wrought and cast alloys gives some clue to the fields of use shown in the earlier part of this chapter. All of the alloys have a combination of properties that are outstanding for the various end uses and account for the large tonnage shown. There is every indication that the present picture will hold for a long time and that copper alloys will continue to occupy a prominent place in our economy.

Chapter 34

Copper and Copper Alloys in the Electrical Industry

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Copper is essential to the electrical industry as we know it today, and likewise the electrical industry is the copper industry's best customer, using approximately 50 per cent of the total consumption of copper in this country. In the years 1951 and 1952 the annual consumption of copper in the United States was close to 1,400,000 short tons. The electrical industry consumed over 700,000 tons, of which the telephone and telegraph industry consumed approximately 100,000 tons.

The reason for this preference for copper is, of course, its high electrical conductivity. Copper has the highest electrical conductivity of any base metal, being exceeded in this respect only by silver. Some steel-reinforced aluminum wire is used for high-tension lines and occasionally aluminum wire is used in BX cable for house wiring. Also steel is used for telephone wires in rural areas, but with these exceptions copper is the predominant conductor material. While copper for conductors appears in many places, it is chiefly used in the form of round wire; however, while the form is usually the same, the size is subject to tremendous variations.

The predominant type of copper in use in the electrical industry is tough-pitch copper; this type combines good mechanical properties and high conductivity at a minimum cost. Occasionally when slightly greater conductivity or ductility is required, oxygen-free high-conductivity copper may be used. The special grades of copper such as phosphorus-deoxidized copper or arsenical coppers are not commonly used for conductors, since they have inferior conductivity.

Other properties which make copper so valuable to the electrical industry are its excellent malleability, tensile strength and yield strength, ease of soldering, and corrosion resistance. Copper can be readily drawn from ⅜-inch rods to 0.003-inch wire without intermediate anneals. The resulting wires are strong enough to be self-supporting under most applications and can be readily joined by mechanical methods or by soldering. Copper also has such excellent corrosion resistance that it is rare that a copper line has to be replaced because of corrosion, and many open-wire lines have been in service for forty years or more.

A physical property which must be considered in the design of apparatus and equipment is Young's modulus. For instance, the tensile yield strength would determine the tension under which a line wire might be strung, but Young's modulus would determine the amount of sag in the line wire under that amount of tension, and would also determine the bow in bus-bar installations.

Another factor which must be considered in design is the thermal coefficient of expansion. The coefficient of expansion of copper is about 50 per cent higher than that of steel and this difference must be taken into account in any design. Thermal expansion is particularly important in line wire and strand installations.

Bare Conductors

Although most of the copper used in the electrical industry is in the form of round wire, the actual uses of the wire are many and varied. Since the greatest use of copper is in the form of transmission wire, this use will be considered first. This wire may be in the form of single-conductor bare wire, it may be multiconductor strand, or it may be in the form of insulated cable. The simplest construction is the single-conductor open-line wire. This wire is normally strung between insulators supported on poles. The installation requires careful consideration of strength, Young's modulus, and coefficient of expansion. Consideration must also be given to the type of terrain over which the wire will be strung, to variations in temperature, to the prevailing winds and expected storm conditions, and to the possibility of sleet. Compromises must be accepted in designing for all these factors. For reasons of economy it is desirable to space the poles as far apart as possible and to string the wire as tightly as possible, since this would require the minimum number of poles and the minimum length of wire. Also it is desirable to use the minimum-size wire which will conduct the required current. However, in order to have a wire perfectly straight between poles it would be necessary for it to have either an infinite Young's modulus or a zero mass. Since copper has an elastic modulus of approximately 16,000,000 pounds per square inch and weighs $\frac{3}{10}$ of a pound per cubic inch, this condition cannot be met. Therefore, the wire can be drawn only to such a point that the maximum stress under the most extreme conditions will be slightly below its yield point. The resultant sag will be a function of the length of the span, the weight of the wire, its modulus of elasticity, and the tension under which it is strung. Furthermore, consideration must be given to the temperature at the time of stringing. If the temperature falls below that at which the wire is strung the wire will tend to shrink and will increase the tension. Consequently, allowance must be made for shrinking so that the wire will not break or stretch. Conversely, if the temperature rises the wire will tend to expand and its sag will increase; the original wire must therefore be strung high enough so that at the time of greatest sag it will not contact other objects or interfere with traffic in the neighborhood.

It can readily be seen that to take all these factors into account at the actual time of installation would require complicated mathematics. Fortunately, all of this material has been calculated ahead of time and linemen are supplied with what are known as sag tables. These tables tell them how much sag to permit in a length of wire of any given diameter between poles spaced any distance apart and at any temperature of installation. In addition to all of these factors allowance must be made for sleet load. In some areas ice as thick as ¾ inch may form on wire and thereby greatly increase the loading. In these areas wire of larger diameter or reinforced wire must be used to carry the added load.

Wire for this type of service will generally run from 0.065 inch in diameter to 0.460 inch. The wires being uninsulated must be spaced at a sufficient distance apart on the crossarms to prevent contact under motion due to wind.

For carrying high voltages and currents, wires which are stranded are usually used. These strands may vary from as few as three wires per strand up to as many as several hundred. The cross-sectional area may vary from 1,000 to 5,000,000 circular mils for this type of service. The size of the strand will generally be adjusted to the current which is to be carried and the voltage loss which can be permitted. The distance between spans is adjusted to fit the size of the wire; the larger the wire the farther apart the supports may be. For any given cross section the type of stranding used will vary to fit the service conditions. The larger the number of wires and the smaller the individual wires, the more flexible the strand will be. Besides the size and number of wires in a strand there is considerable variation in the method of stranding. Wires may have a concentric lay, a rope lay, or a bunch-stranded rope lay. These various constructions are covered by ASTM specifications.

When long span lengths are encountered, copper wire frequently is not strong enough to stand the strains which would be imposed. For such installations steel cores are used both in single-conductor line wires and in multiwire strands. The most widely used method of producing steel-cored copper wire is to cast the copper around a steel core; the composite billet which is produced is then rolled and drawn as if it were a single metal. The wire so produced is much stronger than ordinary copper wire and has a lower coefficient of expansion, but its conductivity is greatly reduced. Two grades of such wire have been standardized, having conductivities of 30 and 40 per cent of that of copper. The cross section of a piece of drawn wire is shown in Figure 34-1.

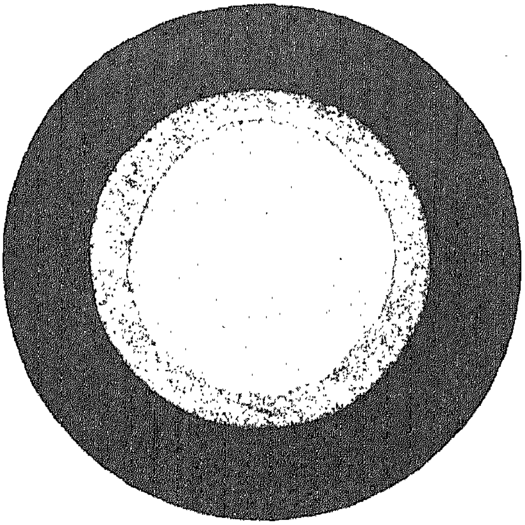

FIGURE 34-1. Cross section of composite copper-steel conductor; conductivity 40 per cent I.A.C.S. (*Courtesy of Bell Telephone Laboratories.*)

The amount of such steel-cored wire used in strands will vary depending upon the length of span and expected weather conditions. There are a number of types of strand made up using steel-cored wire. Usually the strand is so constructed that the steel-cored wires are toward the center of the strand; however, in those constructions which use a large percentage of such wires they may be on the outside. The ASTM specification for such conductors covers strand up to the equivalent of 350,000 circular mils of copper. The actual size of the conductor will be somewhat larger depending upon the percentage of the wires which are steel-cored.

Another form in which bare copper is used in large quantities for the conduction of electricity is known as bus bar. These are the heavy rigid conductors, usually rectangular in cross section, which are used to distribute electrical energy in power stations or substations and in plants of large consumers. The bus bars must be large enough to carry the current imposed on them without undue heating and must also be rigid enough to withstand the inductive pull due to the magnetic field surrounding each bar. Channel sections or tubular bars may be used because of their greater rigidity for carrying very heavy currents with greater distances between supports.

Insulated Conductors

The construction of insulated conductors for power transmission ranges from the very simple to the complex. It is not the purpose of this chapter to describe all of the types of insulated conductors that are used in the electrical industry, since this would require a volume in itself; however, certain of the typical constructions will be described. Probably the simplest insulated wire is what is known as bell wire or annunciator wire. This consists of a single solid conductor insulated with textile or some form of plastic. This wire is used for the transmission of small currents at low voltages for such applications as doorbells and signaling devices. BX cable used in house wiring is another example of a solid insulated wire. This consists of a twisted pair or three conductor wires, each wire separately insulated and twisted together, and enclosed in a wrapping of steel. In some areas a nonmetallic sheath consisting of an impregnated braided covering is used instead of the wrapped steel covering.

Transmission wires as used in local distribution of power are also frequently made of solid conductors which are insulated with rubber or rubber-like compounds and covered with textile braiding. The lead-in or service wires from the street to the customer's property are usually solid single conductor, or they may be twisted pair or three-conductor twisted lines. Insulation on the individual wires may be either rubber or plastic with a braided impregnated covering on the outside.

Where it is necessary to carry larger currents a single conductor becomes so stiff and rigid due to its increased size that it becomes impossible to install. In these cases the conductors will be stranded. These stranded conductors will be similar to those used for bare stranded conductors except that it is common to use a greater number of small wires so that a more flexible strand is produced. The stranded construction is also used for small conductors where considerable flexibility is required. The most common example of stranded construction in small conductors is in lamp and appliance cords. Such cords usually consist of a pair of stranded conductors of either twisted or parallel construction. The individual strands are insulated from one another by rubber or plastic. The completed cord may be covered with textile or the insulation of the strands may be such that the wires are molded together. This type of cord is subject to considerable variation in the size of the individual wires, in the number of wires in the strand, and in the size of the strand. There will also be considerable variation in the kind and thickness of the insulator. However, the basic construction will be the same in that it will consist of two conductors insulated from each other and mechanically bound together.

Cables

The cables which run overhead and underneath the city streets might be said to represent the ultimate in design of electrical transmission members. Aside from the problems involved in installation, these cables are in themselves complex engineering structures. Reduced to the simplest terms, the problem consists of supplying a conductor sufficiently large to carry the required currents, of insulation sufficient to withstand the voltage which will be impressed, and of a covering which will protect the insulation mechanically and will keep out moisture from the environment. In addition, the cable must be sufficiently flexible so that it can be installed and the outer sheath and the entire cable must be strong enough to stand the strains of installation.

The simplest type of power cable will contain a single conductor. This conductor, however, will be made up of many strands. The stranding will vary as discussed under bare conductors. Frequently in order to reduce the space occupied by the conductors so-called compact construction will be used. Under this construction the conductor will be drawn after stranding and in this way the wires will be packed much more tightly than they would with ordinary stranding procedure and the amount of air space within the strand will be greatly reduced.

Alternating currents have a tendency to travel on the outside of a conductor. With the 60-cycle current normally used this effect is negligible on small conductors. However, the effect becomes appreciable on conductors of 1,000,000 circular mils and over. For conductors of this size so-called annular construction is commonly used. In this construction the center of the conductor is made up of rope and the wires are stranded concentrically around the rope, providing the necessary area of copper. With this construction it is possible to decrease the skin-effect ratio for a 4,000,000 circular mil strand from 1.178 to 1.116. However, the over-all diameter of a typical cable will be increased from 2 inches to 3 inches. The choice of the stranding selected for any installation will depend upon such factors as the required flexibility and space limitations.

The insulating material, its thickness, and the method of application can also be subject to considerable variation to suit the conditions of use of the cable, although the most common insulating material for this purpose is paper. Dry paper has high electrical breakdown strength and low dielectric loss, and is relatively inexpensive. Other materials such as varnished cambric are used where a more rugged material is required or for interior applications where the varnished cambric has sufficient moisture resistance so that an outside lead sheathing is not required. Paper-insulated cables are applicable to voltages as high as 69,000 volts. A section of such a cable is shown in Figure 34-2. It may be seen from this illustration that the paper is spirally wrapped in layers around the conductor. Around the outside of the insulation is also wrapped a shield of metallized paper or some nonmagnetic metal foil. On top of the shield is a layer of extruded lead alloy. Lead is used for the cable sheathings because it is impervious to moisture, can readily be extruded around the cable without burning the paper, and is soft and ductile so that the cables can be installed without undue effort. Figure 34-3 shows a similar cable of a larger size in which the conductor is made up of four compacted segments.

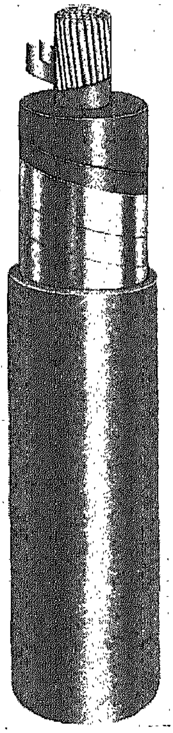

FIGURE 34-2. Paper-insulated single-conductor cable. (*Courtesy of General Cable Corporation.*)

The cable in Figure 34-4 shows the annular construction mentioned previously. The central section of this cable is a rope core around which the copper is wrapped. Concentric core cables are made in sizes up to 4,000,000 circular mils, whereas the annular conductor cables are made in sizes up to 5,000,000 circular mils.

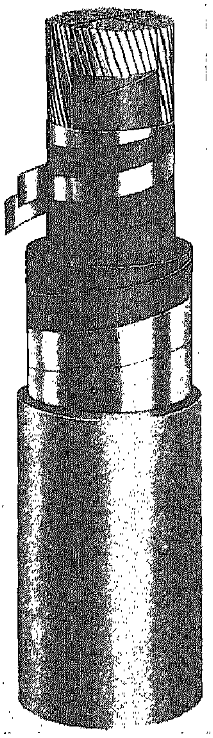

FIGURE 34-3. Paper-insulated single-conductor cable of segmented construction. (*Courtesy of General Cable Corporation.*)

Cables are also commonly made in a three-conductor type. In this case each conductor will consist of a number of wires stranded together. They will usually be compacted into a 120° segment of a circle; each conductor will then be paper-wrapped to provide the necessary insulation between conductors to permit the required voltage. For many applications the individual conductors will be shielded by wrapping metallized paper or metal foil around the outside of the paper insulating layer. Such cables are made for voltages as high as 46,000 volts and in sizes as large as 750,000 circular mils per conductor.

In addition to the solid type of conductor just described, gas-filled cables and oil-filled cables are also made. If these cables are of the single-conductor type, the conductor will have a hollow core through which the gas or oil can be forced. If the cable is of the multiple-conductor type, passageways for the oil or gas will be provided by spirally wrapped tubes which parallel the conductors through the cable. An illustration of such a cable is shown in Figure 34-5. The cable illustrated is an oil-filled

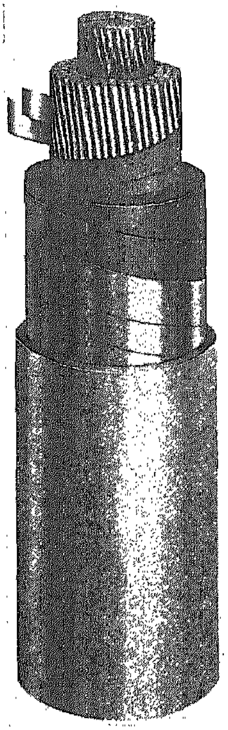

FIGURE 34-4. Paper-insulated single-conductor cable of annular construction. (*Courtesy of General Cable Corporation.*)

cable; if it were gas-filled one of the spirally wrapped tubes would be replaced by a solid walled tube. Appreciably higher voltages may be applied to oil-filled cables than to dry cable. Single-conductor low-pressure oil-filled cables are in operation at voltages as high as 230,000 volts. Three-conductor oil-filled cables are used for voltages up to 80,000 volts. In addition to providing better insulation, both gas- and oil-filled cables provide for supervisory control over the sheath, joints, terminals, and other accessories in that any change in the pressure of the gas or oil will indicate some trouble in the cable. Also the positive pressure of the oil or gas prevents entrance of moisture into the cable through small leaks.

OTHER ELECTRICAL USES OF COPPER

In addition to the many uses of copper in the transmission of power, copper is also important in the generation and use of power. The armatures and fields of generators will always be wound with copper wire. In

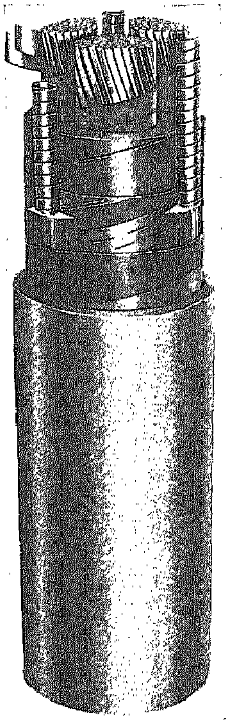

FIGURE 34-5. Oil-filled three-conductor cable. (*Courtesy of General Cable Corporation.*)

the case of armatures, the copper may be of a special shape in order to get as much copper into the space available as is possible. Commutator segments and slip rings on motors and generators are also made of copper. Commutator segments have a special shape to fit into the curvature of the commutator itself. Also the coils of practically all wire-wound apparatus are wound with insulated copper wire, so that while the transmission of power uses the greatest amount of copper, the copper used in the generation and use of the electricity is also of great importance.

The preceding paragraphs are by no means a complete catalog of all the uses of copper in the production, use, and transmission of electricity, but serve to illustrate typical usage of copper in these systems.

COMMUNICATIONS

The communications industry, which is a separate branch of the electrical industry, is in itself a very large user of copper. Many of these uses parallel those in the power industry. Line wire as used in the telephone industry will be similar to that used for power transmission except that

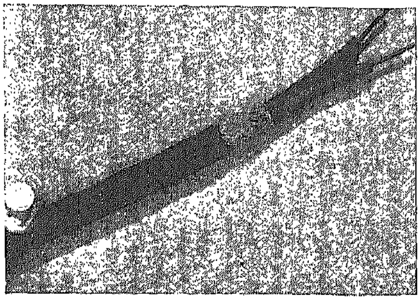

FIGURE 34-6. Telephone drop wire. (*Courtesy of Bell Telephone Laboratories.*)

it will be smaller in size. Likewise the drop wire which is used in carrying current from the telephone lines or cable to the consumer will be similar in construction but smaller than power-service wire. In the telephone industry the heating effects of the currents carried are not usually of much importance, but the drop in voltage along the line is important.

The conductor used in drop wire must have a higher tensile strength than would normally be obtained with hard-drawn copper wire. For many years a copper-tin alloy was used for this application; more recently these conductors have been made of steel-cored copper wire. These drop wires are usually made of parallel-pair, synthetic rubber insulated wire. Figure 34-6 shows a section of this type of wire.

Telephone cable is in many ways completely different from the cable used for power transmission. Instead of being made up of one to four very large conductors, telephone cable may contain up to 2,121 pairs of conductors, each wire being insulated from every other one. Here again paper is the usual type of insulation; however, it is common practice now to form the paper directly on the wire by passing the wire through baths of paper pulp. These individually insulated wires are then stranded to form the completed core of the cable. Each group of wires is individually coded by color for purposes of identification. After the core is formed it is carefully baked to remove moisture, and the cores are then covered with a lead sheath which is extruded in place. An illustration of a section of such a cable is shown in Figure 34-7.

As the frequency of alternating current increases there is a greater tendency for the current to be concentrated on the outside of the conductor. This effect becomes so great in the very high frequencies used for carrier transmission, particularly in the case of television programs, that it is practically impossible to conduct the currents of these high frequencies along solid wires. For this purpose the so-called coaxial line was developed. Figure 34-8 shows a section of a cable containing eight

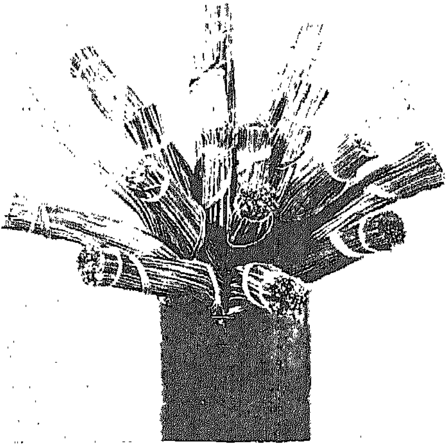

FIGURE 34-7. 1818-pair telephone cable, lead sheathed. (*Courtesy of Bell Telephone Laboratories.*)

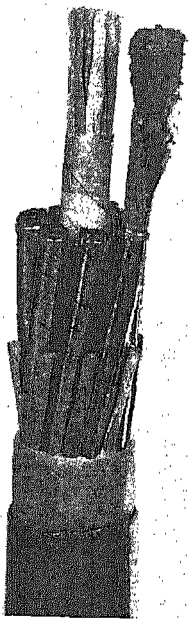

FIGURE 34-8. Telephone cable containing eight coaxial lines. (*Courtesy of Bell Telephone Laboratories.*)

coaxial lines. Each line consists of a solid copper wire in the center around which and insulated therefrom is wrapped a strip of copper to form a tube; around this in turn is wrapped a strip of magnetic material to shield the coaxial line. These coaxial lines are then wrapped around a central core of solid conductors. The central conductors and those in the smaller segmental sections which help to hold the coaxial lines in position contain control circuits for the cable. After this core is formed a thin sheath of polyethylene is extruded over the cable. On top of this a thin sheath of lead is in turn extruded. This composite sheath provides a lighter and more flexible cable than would be obtained with a solid lead sheath and also conserves considerable quantities of lead.

Besides the lead cable sheath shown in these illustrations, telephone cables are now frequently sheathed with a combination of aluminum and polyethylene. To make this cable a corrugated strip of aluminum is first wrapped around the core of the cable and then polyethylene is extruded over the aluminum. This type of construction still further conserves lead. While it was originally introduced for this reason, it has been found to have some advantages in that it is lighter and more flexible.

Another type of conductor used in the communications field for the extremely high frequencies is waveguide. This guide consists of a rectangular tube of some conducting material, usually copper or one of the high-copper brass alloys. The size of the conductor will depend upon the frequency. The higher the frequency, the smaller will be the cross section of the tubing.

As in the power industry, copper is not only used in the transmission of electrical current but is a vital part of most of the electromagnetic apparatus used in the telephone system. The relays which control the signaling and automatic switching systems of the telephone system are operated by coils of copper wire. This wire is usually insulated with enamel, paper, textiles, or plastics or a combination of two or more of these materials.

COPPER ALLOYS

Occasionally special conductors are made from copper alloys. As mentioned previously telephone drop wire is sometimes made of a low-tin bronze. Trolley wire is usually made either from a low-tin bronze or from a cadmium-copper alloy. These alloys are used where greater strength or wear resistance is desired than can be obtained from hard-drawn copper. Such alloys are also used for conductors which are subject to considerable flexing, which might result in fatigue failure.

Copper alloys are used for many applications in the electrical industry which are not primarily conducting. The more common of these alloys are brass, phosphor bronze, and nickel silver. Brass is used in many structural components of electrical apparatus where a medium-strength corrosion-resistant material is required. Some low-stress springs may also be made of brass. However, the greater proportion of springs in the electrical industry are made from nickel silver or phosphor bronze. These two alloys have good corrosion resistance, high yield strength, and high fatigue resistance. The springs of most relays which control the operation of electrical equipment are made of nickel silver. Switch springs and other springs which are subject to considerable deflection are usually made of phosphor bronze. Electrical contacts can be readily welded to either material, or they may be riveted in place.

Occasionally a material is required which has reasonable conductivity with very high yield strength and fatigue resistance. For these applications beryllium copper is frequently used. This alloy has the highest yield strength and fatigue resistance of all of the copper-base alloys and at the same time has better conductivity than the nickel silver and phosphor bronze alloys normally used for contact springs. However, its cost is so great that it is only used where one or more of its unusual properties are required.

Though use of brass-mill products in the electrical industry is small as compared with the large tonnage of copper used, they are an essential part of the industry. Here again the electrical industry is one of the brass mill's best customers and the interdependence of the copper and the electrical industries is again evident.

Chapter 35

Copper in the Building Industry

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Manager, Copper & Brass Research Association

Thousands of years ago, long before recorded history, man discovered that certain kinds of "stone" could be formed into hammer heads. By tapering one end he fashioned a far more practical tool, the axe. After a few centuries he was fabricating this material, later to be known as copper, into a variety of shapes. Spears, knives, and arrow points served dual purposes in hunting and fighting. American Indians of the Northwest may have used such copper wedges to split straight-grained timbers in order to provide planks for their dwellings.

Copper was also known to the Romans. The word is a corruption of cyprium, which the Romans called the metal because most of it was obtained from the Island of Cyprus.

Ancient copper craft got much of its stimulus from the ingenious Egyptians. They developed furnaces for smelting copper and devised a method of producing bronze. Egyptian tombs contained crude pictures of their manufacturing methods and many examples of their products. They actually cast in bronze the great doors of the massive temple of Karnak. This was probably the earliest architectural application of the red metal.

In view of the modern popular use of copper tube it may seem strange that water had been conveyed in copper pipe by the Egyptians; a section of copper pipe nearly 5,000 years old was unearthed in the tomb of the Pharoah Cheops.

The great Roman baths or Thermae, capable of accommodating 3,000 bathers at one time, used bronze pipe. Within recent years Italian government engineers have recovered the barges of the Emperor Caesar Caligula from Lake Nemi, where they had been totally submerged for nineteen centuries. They were large enough to have served as palatial houseboats and were sheathed with copper plates below the water line. The bronze mooring rings and figureheads were in as excellent a state of preservation as were the copper plates.

Copper, due to its high resistance to corrosion, has been used extensively, particularly for exterior application, in building. The cornice around the central opening of the dome of the Pantheon in Rome and the roofs of many of the later castles, palaces, and churches were of copper. The oldest example of copper roofs, the Cathedral of Hildesheim, Germany, erected in 1230, was destroyed by bombing in World War II. But the Palace of St. James, London, built in 1520; Kronberg Castle, Elsinore, Denmark, 1585; and in this hemisphere, Christ Church in Philadelphia, constructed in 1737, may still be admired.

Sheet Copper Work: Roofs

Thus for centuries copper has been the traditional covering for monumental buildings of high intrinsic value. The roof is one of the most important components of a building structure and when properly erected, copper roofs resist indefinitely penetration of rain, snow, and sleet into the interior. When it is interlocked and securely fastened to the undersurface by cleats there are no loose ends for high winds to uplift and tear off. Lightning striking a grounded copper roof can be shunted into the ground by a copper conductor. Sparks and flying embers from nearby fires find nothing to ignite on a copper surface.

There are three general types of copper roofs: batten seam, standing seam, and flat seam. In batten or ribbed seam roofing, the surface is attractively broken up by evenly spaced parallel battens 1¾ inches wide and 20 to 30 inches apart running with the slope of the roof. The sides of the battens have a slight inward taper to provide room for expansion of the cold-rolled copper sheets that fit between them. These sheets are securely cleated to the laying surface and locked into copper caps which protect the tops of the battens. This type of construction can be used on slopes as low as 3 inches to the foot in those parts of the country which do not experience ice and snow. In northern climates the pitch of the roof should be steeper. The pleasing architectural effect of the battens makes this type of roof an excellent cover for the large gable and mansard areas of public and monumental buildings because it combines grace with ornamentation.

In standing-seam construction adjacent pans of cold-rolled sheet copper somewhat similar in shape to those used in the batten type are locked together by a simple joint known as a standing seam, which finishes about 1 inch above the level of the roof. As the sides of the pans are turned up at slightly less than a 90° angle, space is automatically provided for expansion. The standing-seam method is the simplest and most economical method to apply sheet-copper roofing. While it can be applied on slopes as low as 2½ inches to the foot, conditions involving ice and snow require steeper slopes.

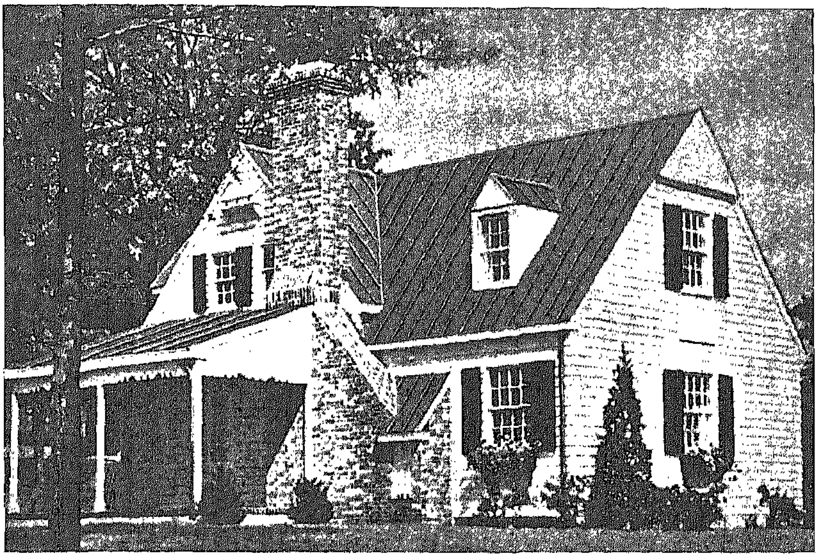

FIGURE 35-1. Copper roofing. (*Courtesy of Copper & Brass Research Association.*)

Batten and standing-seam roofing permit lateral movement between seams and also movement in the direction of the slope. Flat-seam construction does not allow this freedom. Such construction is made up of many small sheets, generally no larger than 16 by 18 inches with ¾-inch seams cleated, flat-locked, and soldered. Each small piece, secured by cleats and stiffened by soldered seams on about 23 per cent of its area, acts as an individual unit and absorbs its own stresses due to thermal change. The pressure of cleats on all four sides tends to disperse the stresses evenly in all directions. However, under the usual cycle of climatic changes unevenly distributed stresses may be introduced. It has therefore been found advisable to divide the roof into panels of approximately 37 by 36½ feet with intermediate expansion battens. Each panel is drained independently. While flat-seam construction is usually used on dead-flat roofs or on slopes less than 2½ inches to the foot, it can also be employed on vertical walls and on the curved surfaces of spires, towers, domes, cupolas, etc., because the small sheets can be varied in size and shape to fit curvature and pattern. Flat-seam construction is also suited for use under artificial lawns, gardens, and terraces built on roofs and for courts, patios, lobbies, entrance plazas, and the like.

When architects desire an unusual surface they frequently resort to crimped copper for such uses as cornices, domes, cupolas, ornamental figures, and formal shapes. Crimped copper has small V-shaped ridges running crosswise to the length of the sheet. These small crimps permit a "bellows" action for expansion and contraction and give a pleasing character to plain surfaces.

Corrugated copper sheets are employed in some applications. They are rolled into a continuous series of longitudinal parallel symmetrical waves usually of a circular arc cross section. The primary purpose of the corrugations is to add strength to the sheets and to facilitate the run-off of rain water.

Copper is an ideal material for spandrels because of its light weight, workability, and pleasing color. It is available in various forms as stamped or formed sheets to suit the needs of the particular application.

Flashing

On the exterior of every structure precautions must be taken to safeguard against leaks at all surface intersections, whether they are vertical, horizontal, curved, or sloped. Because its ductility assures easy fabrication, copper is ideally suited and widely employed as a flashing material. One of its most common applications is in valleys formed by the intersections of roof surfaces of different slopes. They may be of two kinds, open and closed. Open valleys are in more general use and consist of an exposed continuous copper strip which readily conducts water away from the intersection. Closed or concealed valleys, as the name implies, are hidden from view. They are made up of a series of overlapping copper strips set in place as the roofing shingles are laid. The dimensions of the strips are dependent upon the size of the roofing shingle and the slope of the intersection. Closed valleys are to be found on the slate roofs of fine buildings where the architectural treatment calls for soft roof line and closed plane intersections.

The ridges and hips of roofs might be considered the opposite of valleys, but follow either the open or concealed type of construction. The open type lends itself to the use of various ornamental designs.

Gable ends and wall copings serve both an architectural and practical purpose. They outline the structure in a distinctive manner after a period of weathering and effectively prevent water from being blown under shingle edges or from soaking through the tops of the walls.

Unfortunately, the top of a wall is not the only place through which water can penetrate. Modern design has developed the use of comparatively thin curtain walls and hollow-tile construction. Wind-driven rain may seep through face brick and mortar joints and form water pockets which can ruin ceiling and wall plaster. Specially formed copper sheets, known as through-wall flashing, have been designed to provide a very efficient water barrier against this type of penetration. The deformations in such flashing are such that the mortar in contact with them is keyed in all directions to provide a good bond. Tests have demonstrated that the brickwork above such flashings is just as secure as that below them.

When roofs join walls and parapets two types of copper flashings are generally required, base and cap. Base flashing makes a watertight contact with the roofing material at a short distance out from the wall and extends back to and vertically up the wall to an appropriate height. The vertical portion of the base flashing is covered by a cap flashing that extends out of and down the wall to overlap the base flashing. The cap flashing may be locked into a through-wall flashing or secured in a specially constructed reglet in the wall.

Space does not permit a detailed discussion of the many other parts of a structure which require efficient flashing to maintain a weather-tight building, but a few of the more common may be mentioned: doors, windows, skylights, ventilators, scuppers, cornices, wall intersections, and expansion joints.

Gutters and Leaders

The primary function of gutters and leaders is to convey rain water as rapidly as it falls to designated discharge areas. Gutters are of two general types, built-in and hanging. Built-in gutters are a structural part of a building, generally hidden from observation from the ground. Due to the necessity of sloping them in the direction of the downspout they have a variable depth. Experience has shown that stresses set up by thermal expansion in the metal lining of a built-in gutter correspond to those in a loaded column, and that freedom of movement is essential in order to avoid excessive strain. The weight of the copper used therefore must be sufficient to withstand the calculated stresses for a given length and shape. The longer the run the thicker the metal required for the lining. Excessive lengths may be avoided by the use of expansion joints and additional downspouts. Good gutter design requires the use of cold-rolled copper, uncleated cross seams, continuous longitudinal slip joints, a smooth nonadhering undersurface, and transverse expansion joints. Gutter shapes should be deep and narrow, with the sides as steep as possible but not vertical in localities where ice formation may be expected, as a slight angle provides relief in freezing.

Hanging gutters are suspended generally from the eaves of the roof. The pitch is regulated by the length of the hanger straps. A rather wide selection of molded shapes is available. Expansion joints are simple, but except in unusually long runs are not required. Round, square, or rectangular downspouts, either plain or corrugated, may be used. Accessories in the form of corner sections, strainer, leader heads, leader hooks or straps, shoes, and elbows can be obtained readily.

Termite Shields, Screens

The toll of damage caused by termites runs into millions of dollars annually. Termites work their way from the ground into wood sills, joists, studs, and floors of buildings. It is essential in dealing with termites to cut them off from their contact with the ground moisture which is necessary for their survival. A 16-ounce sheet of copper placed over the top of the masonry foundation and extended beyond both sides of the wall forms an effective barrier to termites. Cross seams should be tightly malleted and soldered.

The common housefly and mosquitoes are other forms of pests that cannot get by copper barriers. Bronze screens, highly resistant to corrosion, last practically indefinitely. Before replacing screens in the spring it is advisable to scrub them thoroughly with soap and water. If a light-colored paint is used on the frames the wire cloth may be given a coat of marine varnish thinned out with turpentine, so that the mesh will not be clogged, to guard against staining of adjacent painted areas.

Sheet copper and copper rod are employed extensively in the construction of louvers, ventilators, kalamein doors, lightning rods, dowels, and miscellaneous fasteners.

Hardware

The average person is probably more aware of the use of brass mill products in builders' hardware than in any of its other forms, since brass and bronze hardware has such a wide range of practical applications. This section will briefly touch upon such articles most generally employed in the building industry.

Locks were first used by the Egyptians and later by the Greeks and Romans. In ancient times, the advantageous use of locks was offset by the weight of the keys to be carried. Today, keys are small by comparison and made primarily of brass or nickel silver. They are comparatively light, hard, and sturdy. Brass is used for the locks themselves because of its corrosion resistance and its excellent forgeability and machinability. In many instances small locks are enclosed in a brass doorknob or made an integral part of a door handle. The addition of a brass door knocker, letter slot or mail box, and house numbers adds to the attractiveness of the entrances to many homes.

Other brass or bronze articles which enhance both the appearance and value of a building are hinges, door holders, door closers, push and kick plates, panic bars, window latches, etc. Although this equipment is essentially functional, few decorative pieces are more effective. Bronze plaques, brass or bronze name plates, mail chutes and boxes, and directory listings give a structure a distinguished and substantial appearance. Brass or bronze Terazzo strips, railings, elevator doors, and window frames also contribute to this effect.

A building that is furnished with solid brass hardware is generally regarded as having been well constructed and is more likely to be considered an attractive investment.

Plumbing

The resistance to corrosion of copper and red brass (85 per cent copper, 15 per cent zinc) pipe has long been recognized. Many of our finest buildings have been equipped with copper and red brass hot and cold water lines; the Woolworth building contained 180,000 pounds, the Empire State building 600,000 pounds, and it is estimated that a total of more than 10,000,000 pounds went into Radio City for plumbing, flashing, hardware, and decorative work.

The cost of brass pipe was a problem for the small home owner of a few years ago, but the development of copper water tube with soldered fittings has made available this desirable metal at a cost comparing quite favorably with far less durable materials. Copper water tube does not require extra metal for thread cutting for threaded joints and so can have much thinner walls, saving weight and metal cost with no loss in strength. Soldered fittings fit snugly on the tube. Solder is generally applied to the edge of a fitting after heating and flows completely around the inside surface by capillary action, bonding it to the adjoining exterior surface of the tube. Tests have proved the joint to be as strong or stronger than the tube itself.

Copper tube has been designed to meet service conditions encountered in building construction in the form of three ranges of wall thickness—heavy, medium, and light. Type K, the thick-walled tube, is primarily used to convey water underground from the main to the structure or for other relatively severe service. Because it may have to conform to the uneven contour of a trench it is available in a temper most suitable for bending, namely soft temper. Its walls also are made sufficiently heavy to withstand the effects of back filling. For other uses, hard temper is also available.

Type L is a medium-walled tube suitable for general interior plumbing applications. It is available in both hard and soft tempers, that is to say, it may be obtained in rigid straight lengths or in coils for use where extensive bending or weaving may be required. Hard temper tubes are best adapted for lines hung from ceilings and other installations in which a precise slope for drainage purposes is desired. Soft-temper tube is capable of being bent around obstructions without the use of additional fittings. It is most effective in alteration work, as long lengths can be uncoiled and snaked through walls with a minimum expense of cutting and repairing plaster. It can similarly be drawn under floors and around machinery.

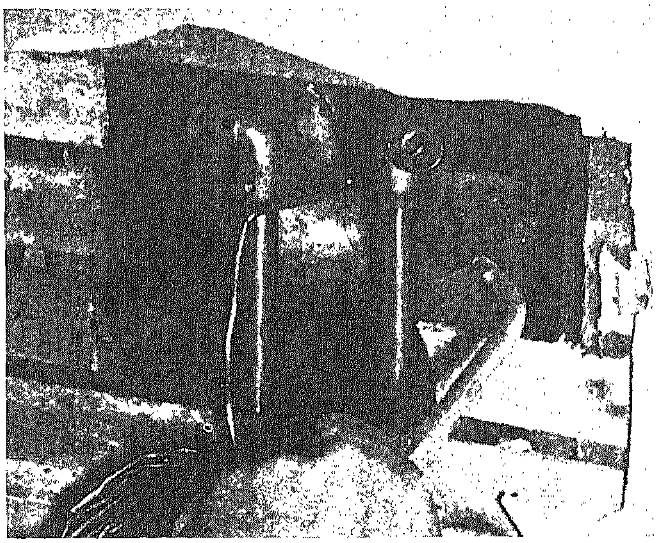

FIGURE 35-2. Advantage of using soldered fittings in a limited space. The fitting is being soldered through a small opening in the ceiling before the tube is put into final position. (*Courtesy of Copper & Brass Research Association.*)

Type M (the thinnest-walled water tube) is available in the hard temper only. It is for use in nonpressure applications, such as heating return lines and sanitary waste and vent lines. Experience with Type M tube for waste and vent service has demonstrated that it is eminently satisfactory in this use. Builders quickly recognized the saving in such installations and architects appreciated the economy in interior wall space. As a result Type M tube with soldered fittings is being extensively installed in the sanitary systems of new buildings. The corrosion resistance of copper tube for hot and cold water supplies and in waste and vent lines assures satisfactory service almost indefinitely.

Many home owners and commercial industrial firms use copper tube to provide an adequate supply of water during the dry season for lawns and gardens. Golf clubs install copper-tube sprinkler systems for maintenance of greens and farmers similarly are using it to irrigate crops.

Although it may not be apparent at first glance because of the chrome plating, most water faucets and many bathroom and kitchen fixtures are solid brass.

Heating

Radiant heating, while not a new method of heating, is just beginning to come into its own. Instead of using radiators, hot-air ducts, conveyors, or other space-taking and dust-collecting devices to radiate heat into the rooms, ductile soft-tempered copper tube is buried under flooring or behind ceiling or wall surfaces. Warm water flowing through these tubes produces a steady, healthful, uniform radiant heat. Walls and floors are thus kept free of encumbrances and openings, permitting the movement of furniture to the most desirable locations.

A novel method of snow removal is similar to the installation for radiant heating. Concrete is poured over copper tube properly placed within the sidewalk or roadway forms, thus providing a means for circulating warm water through the slab and heating the surface sufficiently to melt the snow as it falls and prevent the formation of ice. Antifreeze solutions are recommended when operation is intermittent to prevent freezing of the water in the copper tube.

Copper tube is equally well adapted to the conventional steam or hot-water systems. Hard-tempered tube is usually employed in the supply lines in order to maintain a uniform pitch to the boiler. Domestic furnaces, kitchen stoves, hot-water heaters, and industrial heating plants are generally supplied with gas or oil through copper tubes, because of its suitability and ease of installation. Commercial, public utility, and industrial buildings use copper and copper alloys in boilers and condensers. Years of experience have shown that corrosion-resistant copper-base alloys avoid costly leaks, maintenance, and shutdowns.

Cooling

As greater numbers of people experience the comfort and efficiency of working in controlled atmospheres the demand for air conditioning increases. Theaters, stores, factories, office buildings, hospitals, and even homes are regularly being equipped with modern air-conditioning systems. In some industrial plants such as textile mills, precision instrument shops, and in the manufacture of certain chemicals, control of the atmosphere is essential. Refrigeration of foods, drugs, and many medical items is indispensable for the health of entire communities. Copper has played a very important part in the development of these important factors in our advancing living standards by providing a tube which is corrosion resistant, readily fabricated and installed, and providing for the free flow of refrigerants. Many of the controls are also dependent on copper and its alloys.

Miscellaneous Uses of Copper

The electrical applications of copper and its alloys are discussed in another chapter. Consequently it will suffice here to call attention to the great importance of these in the building industry, not only as regards wiring, switchboards, lighting fixtures, etc., but in a great variety of electrical machinery and appliances. The foregoing discussion applies to the uses of copper and its alloys in the building industry requiring the greatest quantities of the metals. Until an effort is made to itemize the articles that contain copper, one does not begin to realize the importance of this metal in everyday life. Many of the decorative pieces in our homes are of copper or its alloys—fireplace hoods, andirons, accessories, and a host of other objects. Most of the control devices and recording and measuring instruments found in the home or in industrial buildings contain copper in their essential elements. Copper and bronze have perpetuated the work of many a famous sculptor. One has only to visit a city park or village square to observe examples of such art.

Chapter 36

Automotive Applications of Copper and Copper Alloys

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Since the industrial uses of copper, brass, and bronze were well established before the birth of the automobile, it was natural these metals should find application in the engine and other working parts of the early "horseless carriages." The automobile manufacturers, following the practice of the carriage makers of the period, were lavish users of copper and brass for ornamental purposes as well. Ornate and costly headlamps, brightly polished radiator shells, and other exterior trimmings had high sales appeal. Through the years, as new models were brought out, the use of brass for its decorative value gradually disappeared. The increased use of the automobile, its transition from a luxury vehicle to that of utility, the application of the improved electroplating processes permitting the substitution of steel and zinc die castings for the more expensive brass, all were factors in the change in style and appearance of the vehicle during the infancy period of the automobile industry. Even the remaining exterior brass parts were given a more easily polished coating of nickel plating.

The change in appearance of the automobile as affecting the uses of copper was of minor significance in comparison with the mechanical and electrical developments. The adoption of electric lights for headlamps and for illuminating the car interior, the replacement of the hand starting crank by the electric starter, the introduction of the windshield wiper, the cigarette lighter, signal lights, all of these developments and many others substantially added to the role played by copper.

Copper and its alloys possess certain combinations of properties which make them very attractive for a variety of automotive uses. These properties include high thermal and electrical conductivity, good corrosion resistance, good bearing properties, softness, and ease of fabrication. The high heat conductivity is of importance in radiators, heater cores, and oil coolers. The high electrical conductivity is important in the various components of the starting, lighting, and ignition circuits of the car. The good corrosion resistance of these metals makes it possible to use them without added protective films in numerous applications where the metal is exposed to air, lubricants, and coolants. The low coefficient of friction of the alloys against steel and their wettability with petroleum lubricants make them useful as bearing surfaces. The softness of copper makes it especially useful for gaskets and washers where airtight seals are required. The ductility of these metals is of value in the manufacture of parts in which deep-drawing or forming operations are involved. They can be easily soldered and brazed to form various assemblies. Where intricate parts are required, they can be cast and machined, and if high strength is required, forged. In the powdered form, the metals can be compacted and sintered to produce permanently lubricated bearings and various other automotive parts.

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* Mr. Upham is now retired.

The number of parts of the present-day automobile made from copper and copper alloys runs into the hundreds. The total amount of copper and copper alloys used in the recent-model cars ranges from about 25 to 40 pounds per car. Compared with the total weight of the vehicle, or with the weight of some of the other materials used, this amount seems low. The material breakdown of a typical 1950 model 4-door sedan showed that steel and iron accounted for about 83 per cent of the total weight. Rubber, glass, fabric, paper, plastics, lubricants, and other nonmetallics accounted for slightly over 12 per cent. Of the approximately 4.2 per cent representing the nonferrous metals and alloys, copper and its alloys accounted for about ¼, or a little over 1 per cent of the total weight of the car. However, this relatively small percentage value is of sufficient importance to make the automobile industry second only to the electrical industry in the consumption of copper in the United States. In 1950, approximately 6,667,000 cars and 1,334,000 trucks were manufactured in the United States. In producing these vehicles, the industry used about 275,000,000 pounds of copper and copper-base alloys.

AUTOMOTIVE APPLICATIONS

In considering materials for production parts, many factors have to be weighed besides service requirements and costs. Availability is a factor of increasing importance. Under government restrictions due to defense efforts certain metals and their alloys are classed as strategic materials. These conditions may result in the use of substitute materials and treatments, and usually with increased costs, to meet the service requirements with equal success. For these reasons, any lists showing parts made from certain metals or alloys may become obsolete information on relatively short notice. "Copper in the Automobile" as outlined in this chapter covers largely its use under normal conditions, that is, when governmental restrictions are not being imposed.

From the products of the mine to the finished parts, copper and copper alloys pass through many processing steps. The brass mills, the wire mills, and the foundry are "raw material" sources for the manufacturers or fabricators of automotive equipment. The forms commercially available include sheets, strip, plates, wire, bars, rods, tubing, castings, forgings, and rolled or extruded special shapes. Due to the close tolerances and the desirable finish of these various forms, the final parts can often be made with a minimum of fabrication. Automotive usage, therefore, becomes primarily a process of adapting the various basic manufactured forms to parts where the particular physical characteristics of the copper and copper-base metals are deemed necessary or desirable. It is, therefore, practical to group the automotive applications according to the form of the raw material.

Sheet, Strip, and Plate

Fabricated Sheet-metal Parts. The largest single use of copper and copper-base alloys is in the radiator and heater, which accounts for half or more of these metals used in the automobile. Compared with most of the materials, copper is fairly expensive, necessitating a high degree of efficiency in its use. The fact that it can be rolled into very thin gages of sheet or strip, plus the ease with which it can be soldered, further encourages the intelligent designing of unit assemblies, such as the radiator, with good economy of metal. In an automobile radiator core these thin gages of copper and brass result in large cooling-surface areas to dissipate the heat carried by the water. The over-all dimensions of the radiator core of one of the smaller popular makes of cars is approximately 18 by 21 by 2¼ inches. If laid out on a single flat surface, the cooling area of such a radiator would be about equal to that covered by a 9 by 12 rug. In making this computation both sides of fins or spacers have been included, since both function as cooling surfaces.

The essential components of the radiator are the core, the top and bottom tanks, which are equipped with inlet and outlet pipes respectively, a filler neck, overflow tube, drain cock, and a mounting shell or strap. The construction of the radiator cores is especially interesting. Two types are commonly used, the fin and tube type, and the cellular type. Cutaway views of the two types are shown in Figures 36-1 and 36-2.

In the fin and tube type, the lockseam tubes are coated externally with solder and inserted in the horizontal fins. Heating this assembly in a furnace to about 260°C (500°F) serves to bond the components into a rigid structure.

In the cellular construction, strips of metal, roll-formed in various patterns, are solder-bonded to form the water passages. To increase the surface exposed to air, spacers or fins of various designs are solder-bonded between the water passages.

The water passages are usually made of copper or red brass, and, in some cases, of yellow brass. For the fins and spacers, copper is preferable because of its greater heat conductivity. Copper containing approximately 8 troy ounces of silver per ton is generally used on account of its high annealing or softening temperature. The temperature at which the radiator assembly is heated for the soldering operation is higher than the annealing temperature of straight electrolytic copper. By using the silver-bearing copper the stiffness of the original cold-worked metal is largely retained in the finished radiator assembly.

A number of other automobile parts are prepared from sheet metal by drawing, stamping, riveting, soldering, and brazing. These include thermostats, carburetor floats, fuel gages, oil gages, glove-door latches, marine

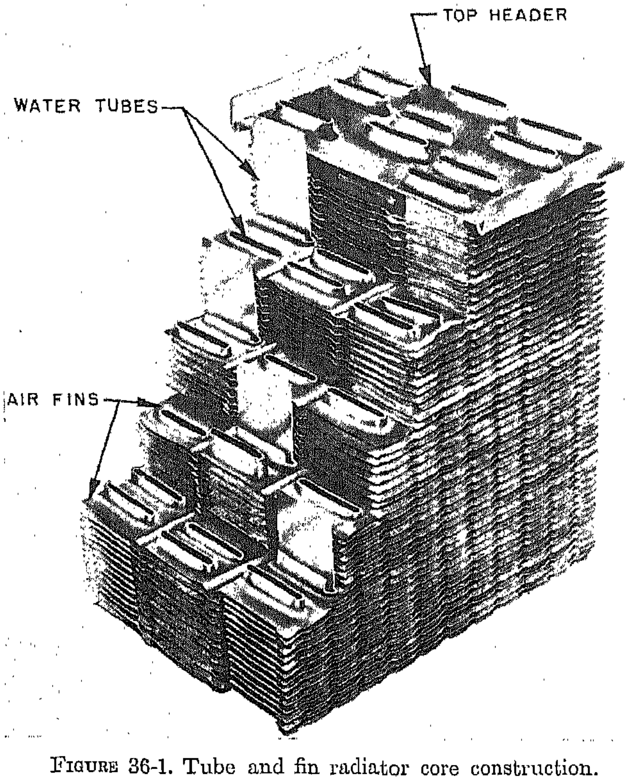

Figure 36-1. Tube and fin radiator core construction.

engine manifolds, and oil coolers. Either copper, red brass, or yellow brass is commonly used for these assemblies. These metals are used primarily because of their corrosion resistance and ease of fabrication.

Simple Stampings. A large number of parts are produced simply by cutting and stamping sheet stock. These include gaskets, washers, spacers, thrust bearings, retainers, gears, springs, housings, dials, and electrical contacts. Yellow brass is frequently used for such parts because of its corrosion resistance and ease of fabrication. Copper is used where a softer metal is required. For simple springs phosphor bronze is usually used. Beryllium copper, though more costly, is favored for severe-duty applications on account of its higher endurance properties. Phosphor bronze is frequently used where low friction is desired.

Ornamental Stampings. A variety of ornamental parts are produced by stamping and embossing, followed by buffing, and with a final finish of either lacquer or nickel-chromium plating. These include bezels, knobs, escutcheons, plates, caps, covers, medallions, and side-view mirrors. Copper and red brass are frequently used in these applications because of the ease of finishing and the excellent appearance of the resulting finish.

Wire

The primary use of wire is in the form of electrical copper. From the standpoint of amount of copper used, this application is second in importance only to that of the radiator and heater. The copper wire is used

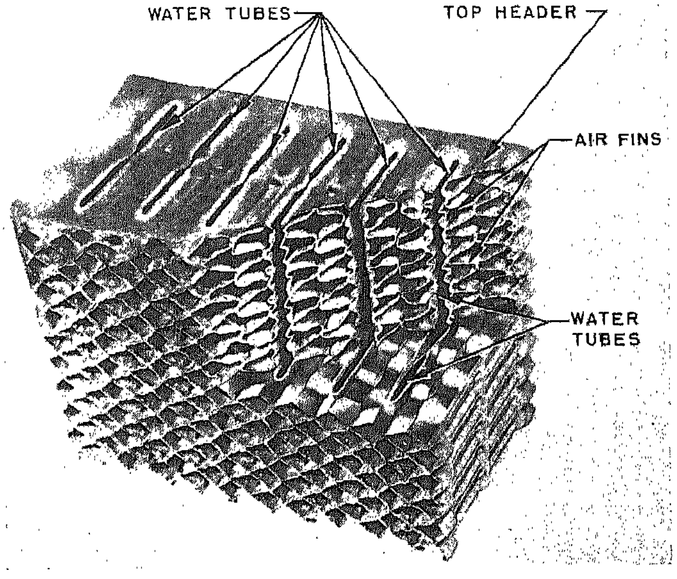

FIGURE 36-2. Cellular radiator core construction.

in the generator, starter motor, windshield-wiper motor, coils, relays, switches, and in wiring for the instruments, lighting, and ignition systems. Since the electrical uses of copper wire are described in another chapter of this book, they will not be discussed here. The secondary automotive usage of wire is in the application of copper, brass, and bronze to such parts as springs, rivets, pins, screens, etc.

Bars and Rods

Bar stock of suitable size and shape may be machined and cold formed to produce a number of different parts. Typical of these are nuts, screws, bolts, elbows, tees, connectors, adapters, studs, rivets, dowels, valve guides, spacers, buttons, knobs, gears, jets, needles, and electrical contacts. Yellow brass, with a small amount of lead added for better machining properties, is most frequently used. Some bronze is also employed for such parts.

Bar stock is used for making commutators for automotive starters and generators, which are mentioned in Chapter 34 in this book. The application is of importance and interest from the amount of copper used, and in view of the special alloys employed to meet the particular requirements.

The commutator must possess a relatively hard wearing surface due to the constant contact with the commutator brushes. It must have a high electrical conductivity as well. These requirements are met by the use of copper of high silver content. Twenty-five troy ounces of silver per ton of copper or 15 troy ounces of silver per ton of copper are the two analyses usually specified.

The commutators are made by blanking segments from the bar. These segments, each separated by thin segments of mica, are then assembled in the form of a ring. The mica and copper are bonded by lacquering and baking at a temperature of about 230°C (450°F). Due to the high silver content the copper does not soften appreciably.

Tubing

Standard tubing sections are used in oil, fuel, brake, and coolant lines, and in radio antennas, instrument assemblies, oil coolers, marine manifolds, heaters, spacers, and sleeves. Copper and red or yellow brass are frequently used in these applications because of their corrosion resistance, heat conductivity, and ease of bending, soldering, or brazing. Due to the cold malleability of these products, watertight and airtight connections are easily achieved and maintained.

Castings

Some automobile parts, due to their design, are best adapted for manufacture as castings. Die castings and permanent-mold castings are the rule for large quantity production of relatively small parts. The traditional sand castings are more apt to be used for comparatively low production items, or for large-sized parts. Typical cast parts include synchronizer rings, lock parts, shifter forks, transmission roller-bearing cages, drain cocks, gears, bearings, hardware, and marine engine castings. Yellow brass, with a small amount of lead added for good machining properties, manganese bronze, red brass, and other bronzes are frequently used for such parts. The desirable properties offered by these materials include good corrosion resistance, good bearing properties, and ease of fabrication and finishing.

Forgings and Shapes

In some applications, usage is made of the excellent basic fabrication properties of copper alloys by means of forgings, pressings, and shapes. In addition to the advantage of minimum material requirements, the high mechanical properties which are characteristic of forgings and shapes are also utilized. Typical applications include gears, transmission shifter forks, synchronizer rings, brake hydraulic pistons, and connector tees.

Metal Powders

Automotive parts having a wide range of properties are produced by the compacting and sintering of metal powders. In addition to copper, other metals used in the powder form include tin, zinc, lead, and iron. Nonmetallics may be incorporated to confer special properties such as the securing of high-friction surfaces or the providing of nonscoring characteristics.

The chief application of metallic powders is for self-lubricated bearings in which the sintered parts are impregnated with either liquid or solid lubricants. Bushings and bearings of this type have wide usage. Typical applications are bearings for transmissions, water pumps, and various electrical units. Examples of the last-named are bearings for distributors, starter motors, generators, windshield wipers, and heater fans.

Applications other than for bearings are fuel filters, various machine parts, and small structural members.

The total number of powdered metal parts in an automobile, and including duplications where several of the same part are used in a car, may total 40 to 60 pieces.

Most of the bearing parts are of copper-base alloy. The others usually contain copper in varying percentages.

Miscellaneous

Present-day automobile practice calls for bright chromium finish of bumpers, radiator grilles, body moldings, door handles, hood and trunk ornaments, interior hardware, and other functional and decorative parts.

These parts may be made of steel, zinc, aluminum, or brass. To secure the necessary corrosion and wear resistance, the plated coatings are held to rigid specifications as to thickness and quality. Standard practice on zinc and aluminum parts is to apply undercoatings of copper and nickel, followed by chromium plating. On steel parts copper may or may not be used as an undercoating. On brass parts the copper plate is usually eliminated.

A special plating application which is of interest is that of brass plating as applied to certain steel parts which are bonded to rubber. Representative of such steel and rubber parts or assemblies are vibration dampers, engine mountings, and clutch and accelerator foot-pedal pads.

Brazing alloys containing a high percentage of copper are used in manufacturing torque converters, fluid couplings, and in fabricating body sheet metal.

A small amount of copper or brass wool is sometimes used as a filtering medium in air cleaners and oil breather caps.

COMPATIBILITY

Compatibility is a service requirement that cannot be overlooked. In use, metallic parts of a motor vehicle have to "live with" lubricants, fuels, hydraulic brake fluids, and engine coolants. Through the years, as a result of much research and development in all industries involved, the problems have been fairly well solved.

Products marketed today for servicing motor vehicles are largely so compounded as to provide the minimum change in composition in use due to contact with metallic surfaces. Also metals used in the manufacture of the vehicles are selected to best meet service requirements of corrosion and wear due to these causes.

Under storage conditions, motor fuels are subject to deposition of gum. Copper is one of the metals that acts as a catalyst in promoting these deposits. While not serious in motor cars and trucks, in marine use it may well be a problem. The use of fuel tanks of copper, unless protected by a surface coating such as tin, is not good engineering practice.

This subject has been given considerable study by the petroleum industry not only as it applies to gasoline, but to lubricants as well. Metal deactivators added to the fuel or lubricant act as protective agents. A substantial reduction in the gum deposits in fuel systems or in sludge in the engines can be achieved by this means.

Hypoid gear lubricants are compounded with definite amounts of certain "extreme pressure" additives to meet the service requirements of this particular type of gear. These additives usually contain sulfur in one form or another. Under the temperature conditions arising in service, these additives form sulfides with copper and to a lesser degree with some of the copper alloys. These "extreme pressure" lubricants are in general use for automotive hypoid axles, and they may also be recommended and used as gear lubricants in other units such as transmissions. Those copper alloys which have been found to be more resistant to sulfur are consequently specified in such gear assemblies.

MATERIAL SPECIFICATIONS

The factors that determine the selection of a particular metal or alloy for a specific automobile part are: (1) service requirements; (2) production or fabrication needs; and (3) costs. Engineering requirements should be, and usually are, interpreted as adequately covering all three factors. The work of the automotive metallurgist has been greatly simplified by the use of the standards and specifications of the technical societies such as the Society of Automotive Engineers and the American Society for Testing Materials. Some of the automotive companies have developed and issued their own material standards.

Standards for copper products were given early attention by the American Society for Testing Materials. The specification on Hard Drawn Copper Wire carries an adoption date of 1909. These technical society standards, in their general acceptance by both the automobile industry and the copper and brass industry, have a commercial importance not fully appreciated. Their scope and use as applied to copper and the alloys of copper are worthy of further study.

Acknowledgment

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Chapter 37

The Use of Copper and Copper Alloys in Ordnance

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The use of copper and its alloys in ordnance can be traced to prehistoric man. Native copper, the first metal used by mankind, was first fashioned into spear tips and axeheads and, with the development of civilization, was formed into knives, arrowheads, swords, and shields. With the advent of smelting and alloying, larger, stronger and more complicated shapes were possible, and when gun powder was discovered, copper-base metals were used to build the first cannons, muskets, and pistols. The development of weapons from muzzle loading to breech loading, then to automatic types of current design, has been dependent on the development of packaged ammunition which, from its early paper containers to present-day cartridges, has relied on copper or brass.

The discussion of the applications of copper to ordnance items will be restricted in this chapter to those uses which are unique and which are not discussed in other chapters. It will suffice to state that the uses of copper-base metals in mobile mounts, jeeps, trucks, tanks, etc., are in general similar to those uses discussed in the chapter on automotive applications. Likewise, the uses of copper and its alloys in field telephones, walkie-talkies, power generators, distribution systems, radios, radar, etc., are similar to those discussed in the chapter on electrical applications.

The role of copper and its alloys in ordnance throughout civilization has been dependent on its ability to be readily fabricated into complex shapes and on varying its mechanical properties. Malleability and work hardenability are two outstanding characteristics which permit the development of the various properties required in ordnance items such as copper crusher cylinders, rotating bands, bullet jackets, bearings, springs, detonators, fuse parts, primer cups, cartridge cases, etc. However, even these items may be made of substitute metals when the unbalanced economics of war create shortages of material and processing facilities.

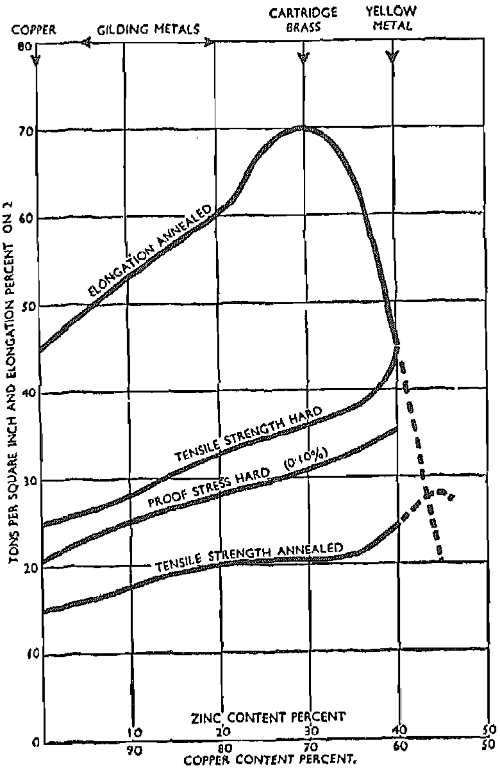

FIGURE 37-1. Curves illustrating the general influence of the Cu-Zn ratio on the mechanical properties of alpha brass sheet.

The largest use of copper in ordnance has been in cartridge brass for ammunition, and this use of copper will be discussed here to demonstrate the extreme variations in properties which can be achieved. Cartridge brass is a 70 per cent copper, 30 per cent zinc alloy, possessing the best combination of strength and ductility of all the alloys in the copper-zinc system. Figure 37-1 shows the influence of composition upon these mechanical properties. Inasmuch as the addition of almost any element to the copper-zinc system tends to shift the solid solubility of zinc in copper as well as change the recrystallization and grain-growth characteristics, the composition of cartridge brass has been rigidly specified by the Government to assure uniformity of properties and working characteristics. It is commercially available under the American Society for Testing Materials specifications B 19-51T and B 129-51.

The necessity of rigidly controlling the chemical composition and thus the mechanical and physical properties of cartridge brass is best demonstrated by reviewing the principal functional requirements of an adequate cartridge case, the method of manufacture, and the properties necessary for the cartridge case to function satisfactorily.

The major functions of a cartridge case are that it shall (1) carry the component parts, (2) have good corrosion resistance, and (3) perform properly in the gun.

The function of carrying component parts is obvious. It includes carrying the propellant, the primer, and the projectile; retaining the relationship of the parts to one another; and protecting each from damage during storage, transportation, and handling. The propellant must not abrade the case and must be confined to a given volume. The primer must be protected from accidental firing and rigidly held in position for firing. The projectile must be held in alignment as well as retained in the mouth of the case.

The function of providing good corrosion resistance includes the ability to withstand long storage and not react with the powder and primer components, since any internal corrosion would affect the ballistics of the round. In addition, the case must resist atmospheric corrosion so that it will chamber and function properly when fired. The case must protect the primer and propellant from moisture and other atmospheric components that would affect their stability or burning characteristics.

The proper performance of the cartridge case in the gun is not as obvious as the other two requirements. First, the case must fit the chamber of the gun with minimum dimensional clearance both diametrically and longitudinally so that it will seal against the chamber and prevent leakage of the hot gases generated when fired. The case must expand on firing to transmit the gas pressure to the gun chamber and to expand with the gun chamber. The case must recover to a size smaller than the gun chamber so that it can be easily extracted. The expansion must be sufficiently fast and recovery sufficiently slow to prevent gases from escaping into the chamber and out of the gun breech. The side wall of the case must vary in properties so that the obturation progresses rearward from the mouth to the head in order that the case can expand longitudinally and follow the mechanical and elastic yielding of the breech.

The head of the case must be rigid enough to permit the primer to obturate properly during firing and to retain it in place. However, the head must be ductile enough to permit some expansion at the side-wall junction.

A cartridge case can perform the foregoing functions without failure when it is properly designed, made of the proper metal, and fabricated by the proper techniques. The design of the case is usually controlled by

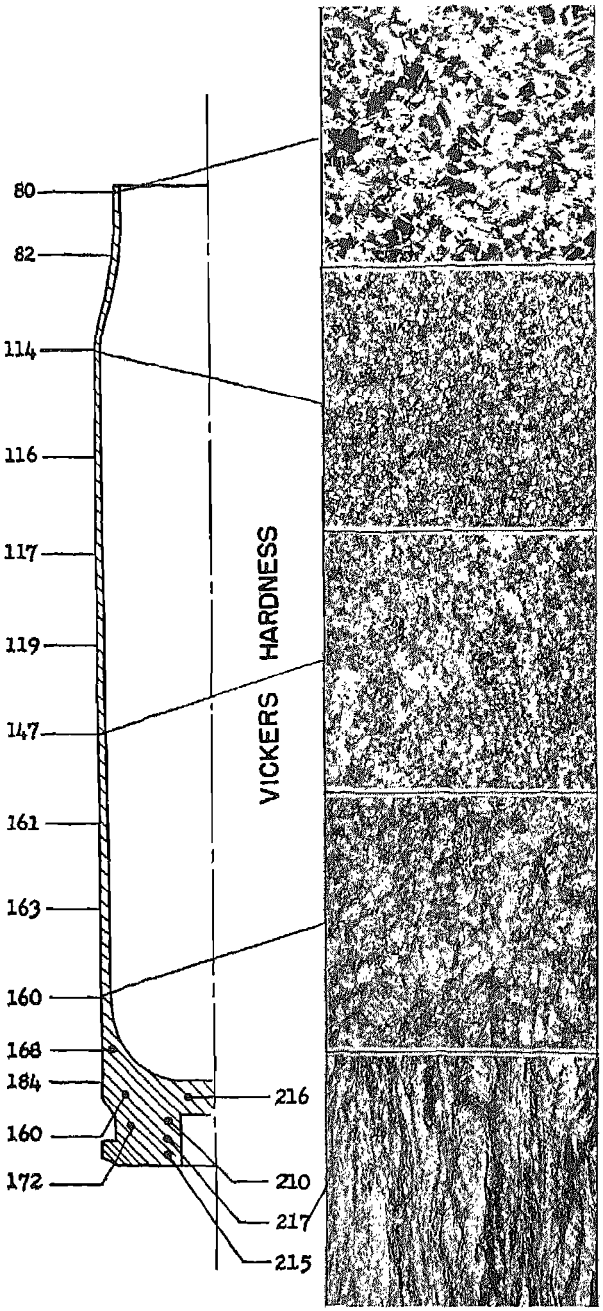

FIGURE 37-2. Hardness survey and microstructure of caliber .50 brass cartridge case. Etched with $H_2SO_4 + K_2Cr_2O_7$. Magnification 60X.

the chamber and ballistic requirements of the gun. The metal for the case is selected on the basis of the properties obtainable and the ease of manufacture. The fabrication techniques are selected on the basis of properties to be obtained and the economy of operations.

Brass with its inherent properties of high impact strength, wide range of strengths and ductilities, intermediate modulus of elasticity, good corrosion resistance, and excellent workability is a natural cartridge-case metal. Other metals can be substituted at a sacrifice of performance or economy.

The properties needed in a brass cartridge case, shown in Figure 37-2, can be obtained by a combination of proper design and manufacturing technique. The design of a case is usually a tapered side wall with varying mechanical properties and a thick head with an odd contour and sharply changing properties.

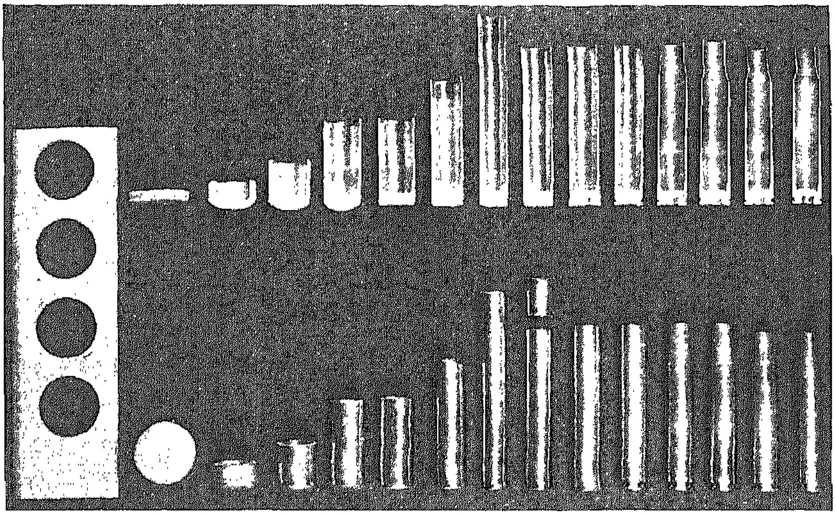

FIGURE 37-3. Process pieces in the production of a caliber .30 brass cartridge case. One-third actual size.

1. Strip. 2. Blank. 3. Cup. 4. First draw. 5. Second draw. 6. Bump. 7. Third draw. 8. Fourth draw. 9. Trim. 10. Head. 11. Head turn. 12. First taper. 13. Second taper. 14. Final trim. 15. Vent.

Cartridge cases are normally made by a cup-and-draw process, a typical schedule of which is shown in Figure 37-3. The strip used in this process has a closely controlled grain size and a thickness which is dependent on the final head thickness of the finished case. The blanking and cupping operations are frequently combined into one through the use of a double-acting press. An annealing operation is used to condition the metal for the subsequent deep-drawing operations in which the sinking and ironing frequently result in as much as 60 per cent reduction in side-wall volume. Each of the drawing operations except the last is followed by an anneal. A bumping operation frequently is used to flatten the base of the draw piece in order to hold the metal in place and to preform the head.

Tapered punches are used in drawing to produce the tapered side wall of the case. A heading operation, which follows the final drawing operation, cold works the base metal as it forms the primer pocket. The head-turning operation is a contour machining operation prior to the taper anneal which softens only the upper side wall of the case piece. The tapering operations are used to taper the case from head to shoulder and to form the shoulder and mouth of the case. A final trim to control the over-all length of the case is followed by a venting operation in which the flash hole between primer pocket and case cavity is pierced in the web. The last operation is a mouth anneal which softens the neck of the case so that it will function satisfactorily when a bullet is assembled in it.

The properties needed in a cartridge case to enable it to function properly vary with each position of the case and the design used for the particular case under consideration. There are five distinct locations in a cartridge case, as shown in Figure 37-2, which vary in properties relatively independently of design.

(1) The neck or mouth of a case is usually annealed to permit plastic deformation when the bullet is inserted and crimped in position, with a minimum resultant stress, thus preventing stress-corrosion cracking. Contrarily, the neck must be sufficiently rigid to hold the bullet in alignment and to yield a high bullet-pull for handling purposes while a tight seal is maintained between the neck and the bullet to protect the propellant powder from the atmosphere. Generally a fine grain size and low hardness, as shown, and a tensile strength of the order of 45,000 to 50,000 psi are satisfactory.

(2) The side wall just below the shoulder is normally a lightly worked annealed structure resulting from the tapering of the case after the upper side wall has been given a taper anneal to allow the formation of the shoulder and neck. The grain size is small, the hardness is relatively low, and the tensile strength is of the order of 50,000 to 55,000 psi.

(3) The mid side wall of a case is usually a partially recrystallized worked structure resulting from the taper anneal blending into the worked lower side wall. The grain structure is duplex, the hardness is relatively high, and the tensile strength is of the order of 70,000 to 75,000 psi.

(4) The lower side wall of the case is heavily cold worked as a result

of the final drawing operation. The grain size is indeterminate, the hardness is very high, and the tensile strength is of the order of 85,000 to 95,000 psi.

(5) The head of the case is usually of mixed properties as indicated by the hardness variations shown in Figure 37-2. The side wall of the primer pocket is the hardest section of the case, since it must retain the primer cup and maintain a tight seal when the cartridge is fired in the gun as well as during handling and storage. The grain size is indeterminate, the hardness is extremely high, and the tensile strength is of the order of 105,000 to 110,000 psi.

From the foregoing details, it can be seen that a cartridge case to function properly must be fabricated of a metal possessing excellent workability. Also, an extremely broad range of physical properties must be obtainable through an economical fabrication procedure. Cartridge brass has these required characteristics.

The second largest use of copper in ordnance has been for projectile rotating bands, which are usually made of pure copper or gilding metal of 90 per cent copper, 10 per cent zinc. Both of these metals are rigidly specified by the Government and are commercially available under American Society for Testing Materials Specifications B 75-51T and B 130.

The properties required in a rotating band are good bearing, engraving, and shear properties together with low resilience, since the band must engrave readily, spin the projectile, and not wear the barrel of the rifle when the projectile is fired.

Other ordnance items, namely, fuse bodies, detonators, copper crusher cylinders, primer cups, etc., require different combinations of properties such as corrosion resistance, machinability, and strength; low yield strength, low elastic modulus, and high elongation; resilience, toughness, and strength, together with ease of manufacture and uniformity.

Stated concisely, copper and its alloys are used extensively in a very wide range of ordnance items because they can be readily fabricated to meet service requirements on a favorable cost basis.

Chapter 38

Copper and Copper-Zinc Alloy Plating

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Copper is electrodeposited from both acid and alkaline electrolytes. Copper sulfate and copper fluoborate are acid electrolytes. Copper cyanide, copper pyrophosphate, and copper amine are alkaline electrolytes. The copper sulfate and all three alkaline baths may be operated under conditions to give bright deposits requiring little or no buffing in order to obtain a satisfactory quality of surface finish. The alkaline bright copper processes are more commonly employed for producing bright copper deposits on steel or zinc die-cast objects to which bright nickel and chromium coatings may be subsequently applied without the necessity of first buffing the intermediate copper coating. This eliminates the cost of buffing the copper, the loss of the copper thickness removed by buffing, and the cost of reracking and cleaning prior to bright nickel and chromium plating.

The alkaline copper baths have much better throwing power than do the acid baths. In other words, it is easier to plate a given thickness of copper into a recessed area of an irregularly shaped object using an alkaline bath. It is also for this reason that the cyanide copper bath is universally used for barrel plating applications.

It is possible to use higher current densities with the acid baths and even though the copper is deposited from the divalent state, as compared to the monovalent copper cyanide bath, the rate of deposition can be much higher. Greater thickness can also be deposited from the acid baths without loss of desirable properties. These baths are, therefore, the ones mostly used in electroforming of copper objects and for copper coating of steel wire for electrical applications.

The acid copper sulfate bath, when operated under conditions to give bright or semibright deposits, is also extensively used in plating objects made of low-carbon cold-rolled steel with copper as an undercoat for bright nickel and chromium protective coatings. Innis reports[1] that if the surface finish of the steel is about 10 microinches (RMS), a bright acid copper deposit of 0.001 inch will reduce the surface finish to 4 to 6 microinches, and under these conditions it is not necessary to buff the copper prior to plating with bright nickel and chromium. It is also quite common to omit any polishing or buffing of a reasonably smooth steel basis metal and to deposit a bright or semibright acid copper coating which is then buffed to give the required surface luster prior to bright nickel and chromium plating. This latter procedure offers a substantial saving in cost while attaining a high quality of finish.

Periodic reversal of the direct current during plating from a cyanide copper bath, such as in the Wes-X PR process[2, 3], has been used in the electroforming of sound-recording records stampers, printing rolls, and textile rolls with excellent physical properties. However, the acid copper baths have long been used in the production of such items and for electrotypes and other electroformed objects[4, 5]. It is too soon to state to what extent the Wes-X PR process will be applied in electroforming. As a means of producing a bright copper deposit of uniform thickness with a high degree of leveling[6, 7], *i.e.,* reduction of the surface roughness of the basis metal, and as an undercoat for bright nickel and chromium protective coatings, without the necessity of prior buffing of the copper, it offers attractive possibilities. In several installations of this kind using current densities of 100 amp per square foot copper is deposited faster and brighter than from bright acid baths.

Deposits of copper from cyanide baths are extensively used as a means of preventing carbon penetration on selected areas of steel objects during case hardening[8]. The thickness of the copper coating for the latter purpose must be increased as the required depth of case hardening of the exposed steel surface is increased. This is a function of the time and temperature of the hardening process. For most purposes coatings from 0.0005 to 0.001 inch are adequate. Porosity of the coating is an important factor which can be reduced by increasing the thickness. A rapid plating process of high current efficiency is favored.

Cyanide copper deposits serve as a base for ornamental finishes or subsequent plating with other metals such as nickel and silver. Thin copper coatings are used as an aid in the drawing of steel. These may be deposited from a cyanide copper bath or by a copper immersion process. For immersion coatings a bath containing 2 oz per gal (15 grams per liter) of copper sulfate crystals and 1 fluid oz per gal (7.7 ml per liter) of sulfuric acid may be used.

In selecting a copper plating process for a given application the permissible thickness of the coating, the required brightness and properties of the deposit, the cathode efficiency, the throwing power, the degree of leveling attainable, the allowable rate of deposition, and the required materials of construction for the tanks, piping, fitting, pumps, filters, and heating or cooling equipment are all important considerations. Sometimes the requirements for waste treatment may also be a controlling factor.

Plating on Ferrous Metals

Copper cannot be deposited directly on ferrous base metals from any acid copper bath or any high-efficiency bright alkaline bath without first applying a copper (strike) deposit (0.0001 inch minimum thickness) from a low-efficiency cyanide copper bath. Otherwise copper deposits by immersion, causing poor adherence and, in the case of acid baths, loose particles of copper which cause roughness. Typical cycles[9] for plating copper on low-carbon steel would be as follows:

Typical Plating Cycles for Steel

For Acid Copper	For Alkaline Copper
1. Alkali clean (anodic)	1. Alkali clean (anodic)
2. Warm rinse	2. Warm rinse
3. Cold rinse	3. Cold rinse
4. Acid dip (HCl or H_2SO_4)	4. Acid dip (HCl or H_2SO_4)
5. Cold rinse	5. Cold rinse
6. Cyanide copper strike	6. Cyanide copper strike
7. Cold rinse	7. Cold rinse
8. Acid dip	8. Alkaline copper plate
9. Cold rinse	
10. Acid copper plate	

Plating on Zinc-base Die Castings

Acid copper deposits are not normally applied to zinc-base die castings. Before applying copper to zinc die castings from the high-efficiency, bright, alkaline copper baths a copper strike coating from a low-efficiency cyanide bath must first be deposited in order to prevent an immersion coating of copper which would cause poor adhesion and subsequent blistering of the deposit. A typical cycle[10] for plating copper on zinc-base die castings, such as "Zamak" No. 3 and No. 5 alloys, would therefore be as follows:

Typical Plating Cycle for Zinc Die Casting

1. Soak clean or degrease
2. Spray wash
3. Alkali clean (anodic)
4. Water rinse
5. Acid dip (1 per cent H_2SO_4 by volume until gassing just begins)
6. Water rinse
7. Cyanide copper strike (0.00005 inch)
8. Bright cyanide copper plate (0.0002 to 0.0003 inch minimum as per specification)
9. Water rinse
10. Alkali clean (anodic)
11. Water rinse
12. Acid dip (1.5 per cent H_2SO_4 by volume, 5 seconds)
13. Water rinse
14. Bright nickel plate (thicknesses per specification)
15. Water rinse
16. Chromium plate (0.00001 inch minimum)
17. Water rinse
18. Hot rinse

Steps 8 to 13 in the above cycle would be altered if proprietary alkaline bright copper processes other than the cyanide type were used.

Acid Copper Sulfate Bath

The acid copper bath as given below contains copper sulfate and sulfuric acid. The concentration of each constituent is not critical and is limited only by the solubility of copper sulfate at various acid concentrations.

Acid Copper Sulfate Bath

Copper sulfate, $CuSO_4.5H_2O$	26—33 oz per gal (195—248 grams per liter)
Sulfuric acid, H_2SO_4	4—10 oz per gal (30—75 grams per liter)
Temperature (°F)	70—120
Current density, amp per sq ft	20—100
Agitation, optional but preferred	Air
Cathode efficiency, per cent	95—100

Agitation is essential for operation at the higher current densities. Addition agents such as phenolsulfonic acid, glue, molasses, etc., are frequently added to produce finer grained and smoother deposits. By so doing, the deposits are easier to buff to a high luster. For very heavy deposits it is desirable to filter continuously, particularly when using air agitation, and the anodes should be bagged or a cloth diaphragm[11] should be used to prevent anode particles from causing roughness.

The bright or semibright acid copper processes are sulfate baths to which brightening agents have been added. The luster of a deposit from such baths depends upon the quality of the surface finish of the basis metal and a close control of all operating variables to give a fine grained, smooth deposit. The concentration of the addition agents must be carefully maintained within stated limits and the combination of a relatively low bath temperature with high current density and strong but uniform agitation is usually recommended. Continuous filtration of the bath and the use of cloth anode bags or diaphragms[11] are essential.

The best known bright or semibright acid copper processes are given in Table 38-1. The air-agitated Day-Brite 40 process[12] is for high-speed plating. The Day-Brite 30 process[12] employing rod agitation is used for other applications. The GM process[12, 13] is similarly used. They have all been extensively used to deposit copper, 0.001 inch and upward in thickness, on steel as an undercoat for bright nickel and chromium. The copper is usually buffed prior to nickel plating, thereby obtaining the desired surface finish and sometimes eliminating entirely the necessity for any surface finishing of the steel basis metal. As mentioned previously, it has also been possible to omit the intermediate buffing of the copper coating provided the surface finish of the steel is of sufficient smoothness[1].

TABLE 38-1. BRIGHT AND SEMIBRIGHT ACID COPPER BATHS

Composition	Day-brite* No. 40 oz. per gal.	Day-brite* No. 30 oz. per gal.	GM** oz. per gal.
$CuSO_4.5H_2O$	32	26	33
H_2SO_4	8	5	4
Dextrin, yellow	0.008	....	....
HCl	0.002	0.04	....
Brightener	DB-41 0.006	DB-30 0.003	Molasses 0.1
Stabilizer	....	DB-40 0.30	Thiourea 0.0013
Wetting agent	"Duponol" 80 0.1 ml per gal.	DB-20 0.8% vol.	Triton 720 0.03
Conditions			
Temperature (°F)	80—100	80—85	70
Current density, (amp per sq ft)	75—100	4—70	50—75
Agitation	Air	Rod 20 ft per min	Air
Cathode efficiency, per cent	95—100	95—100	95—100

* Dayton-Bright Copper Company, Dayton, Ohio
** General Motors Corporation, Detroit, Mich.

Lead is commonly used as a material of construction in acid copper sulfate plating baths. Rubber or plastic linings for tanks and auxiliary equipment are preferred.

Fluoborate Copper Bath[14]

Because of the high solubility of copper fluoborate, it is possible to prepare fluoborate baths with much higher copper concentration than with the sulfate bath. At concentrations comparable with the latter bath, higher current densities are possible. At still higher metal concentrations, especially with good agitation, extremely high current densities may be used. Advantage is taken of this in the continuous plating of steel wire. The bath has been used extensively in electroforming. The deposits are fine grained, ductile, and easily buffed.

Copper fluoborate is sold in concentrated solution only, since the dry salt cannot be prepared. In making a bath, it is only necessary to dilute the concentrate with water to the desired metal concentration. Two typical bath compositions and the recommended operating conditions are given below:

	Low Metal	High Metal
Copper fluoborate	30 oz per gal (225 grams per liter)	60 oz per gal (450 grams per liter)
Copper equivalent	8 oz per gal (60 grams per liter)	16 oz per gal (120 grams per liter)
pH, colorimetric	0.8—1.4	0.6
Temperature (°F)	80—170	80—170

Gravity, °Bé at 80°F	21—22	37.5—39
Cathode C. D., amp per sq ft	75—125	125—250
Tank voltage, volts	3—5	4—12
Agitation, optional	Air-Rod	Air-Rod

Materials of construction for use with the fluoborate bath include rubber, plastics, and "Karbate." Lead and duriron cannot be used. "Karbate" and "Worthite" have been used for pumps.

Cyanide Copper Baths

Typical cyanide copper bath compositions are given in Table 38-2. The bath concentrations may be varied from those given, but the metal content, pH, free cyanide, and addition agents must be controlled by analysis for uniform operation. Too low a free-cyanide concentration causes loss of anode efficiency. Too high free cyanide decreases the cathode efficiency. High-purity rolled, cast, or electrolytic copper anodes must be used. The anode area should be about twice the cathode area for high efficiency and satisfactory control of the bath.

The regular cyanide bath (No. 1) and the Rochelle salt bath (No. 2)[15] in Table 38-2 are relatively low-efficiency copper cyanide baths and as such are used as copper striking baths prior to plating steel or zinc-base die castings in the high-efficiency acid or alkaline copper baths. They are not ordinarily used for depositing copper much in excess of 0.0003 inch in thickness. The other baths given in Table 38-2 are high-efficiency bright copper proprietary processes and are used for depositing thicknesses from 0.0003 to 0.0008 inch as required by plating specifications[16] and even greater in certain cases. A minimum copper thickness is always specified as an undercoat for nickel-chromium protective coating for zinc-base die castings as a means of eliminating defects caused by diffusion of thin copper coating into the zinc basis metal[16a]. The copper in this case also prevents attack of the zinc during nickel plating.

With a high-quality surface finish of the basis metal, deposits from the bright cyanide baths are extensively used without the necessity for buffing and reracking prior to bright nickel and chromium plating.

TABLE 38-2. TYPICAL CYANIDE COPPER BATHS

Composition	No. 1 Low Copper oz per gal.	No. 2 Rochelle Salt oz per gal.	No. 3 Bright[1] Potassium oz per gal.	No. 4 Bright[1] Sodium oz per gal.	No. 5 Bright[2] "P.R." oz per gal.
CuCN	3.0	3.5	8.0	16.0	10.0
NaCN	4.5	4.6	12.5*	18.0	12.6*
Na_2CO_3	2.0	4.0	....	....	2.0*
Rochelle salt	....	6.0	....	....	....
NaOH	To pH 12—12.6†	To pH 12—12.6†	5.6*	4.0	6.0*

TABLE 38-2. TYPICAL CYANIDE COPPER BATHS (*Continued*)

Analysis					
Copper	2.1	2.5	5.6	11.3	7.0
Free NaCN	1.0	0.8	1.0*	0.5	1.0*
Additions	**	....	RH774 0.2	RH556 0.2 NaCNS 0.2	Wes-X
Conditions					
Temperature, °F	90—110	130—160	170—180	170—180	180
C.D., amp per sq ft	10—15	20—60	30—60	30—60	30—100
Cathode efficiency, per cent	30	50	100	100	100‡
Agitation	Rod	Rod	Rod	Rod	Rod-Air

[1] Du Pont

[2] Hanson Van Winkle Munning Co., used with various cycles of periodic reversal of direct current.

* Potassium compounds

† Colorimetric pH.

‡ Without PR current; less depending upon PR cycle employed.

** Lead (0.003 to 0.004 oz per gal) or "Hypo" ($Na_2S_2O_3.H_2O$) have been added to brighten the deposit but are not recommended for a copper strike.

Baths 3[17], 4[17], and 5[2] are proprietary processes. Other bright-plating proprietary cyanide processes are Rocheltex[18], Wico Brite Copper[19], and Lea Copper Glo[20]. The first named is a modification of bath No. 2 with an addition agent; the second is similar to bath No. 4 in Table 38-2 with the exception that 50 ml/gal. of WCM Brite Copper serves as the addition agent. The last and most recently announced process is a modification of bath No. 2 employing special addition agents.

Steel may be used for tanks and auxiliary equipment. Rubber or plastic linings are preferred. Lead cannot be used.

Pyrophosphate Copper Process[21]

The pyrophosphate copper bath is made up from proprietary chemicals and usually contains from 3 to 5 oz/gal. of copper as the divalent ion, 20 to 40 oz/gal. of pyrophosphate, and a small amount of added ammonia. The operating conditions are as follows:

pH, colorimetric	8.0—8.5
Temperature, °F	110—140
Cathode current density, amp per sq ft	10—70
Anode current density, amp per sq ft	20—100
Tank voltage, volts	2—5
Agitation	Air
Cathode efficiency, per cent	100

This bath may be used for plating zinc-base die castings as a bright copper process, omitting buffing of copper prior to bright nickel and chromium plating. Agitation is most important for maximum brightness. The approximate amount of air required per square foot of solution surface is 1.0 to 1.5 cu ft per min at 3 psi.

Steel, cast iron, and stainless steel are satisfactory materials for filters, pumps, piping, and heat exchangers. Rubber-lined tanks are recommended.

Amine Copper Process[22]

The amine copper process has been used for plating bright deposits on zinc-base die castings and steel prior to bright nickel and chromium plating. The bath composition and operating conditions are as follows:

	Oz per Gal.	Grams per Liter
Copper sulfate, $CuSO_4.5H_2O$	16	120
Diethylene triamine, 88 per cent	16	120
Ammonium sulfate, $(NH_4)_2SO_4$	2.5	19
Ammonia, 28 per cent	4.0	30
"Tergitol" 08	0.3	2.25
pH, electrometric	9.5—10.5	
Temperature, °F	130—150	
Cathode current density, amp per sq ft	30—50	
Agitation	Cathode or solution movement	
Cathode efficiency, per cent	95—100	

Rubber or plastic is recommended for lining tanks and filters. "Karbate" or duriron is satisfactory for heat exchangers. A duriron pump may not be used for solution circulation and filtration. Piping and fittings should be lined.

Continuous filtration is recommended with periodic carbon filtration and electrolytic purification at low current density to remove impurities.

COPPER-ZINC ALLOY PLATING

Yellow brass and light or red bronze-colored alloys of copper and zinc are deposited from cyanide baths. The color is varied by controlling the percentage of zinc in the deposit. The color of the deposit as it comes from the plating bath differs from the true color of the alloy, as shown by buffing the deposit. It is more difficult to deposit an alloy of copper and zinc than to deposit either metal singly. This is largely due to the complex chemistry of zinc in the baths employed[23] and to the necessity of codepositing copper and zinc in definite percentages.

These alloys are commonly applied to steel, zinc-base die castings, and white-metal alloys to produce brass, bronze, and sometimes gold colors. If applied over a bright nickel coating, only a bright flash coating is required, and this must subsequently be lacquered for protection. More recently periodic reverse plating has been used to produce bright brass deposits of greater thickness (0.0001 to 0.0002 inch).

Brass and bronze coatings are applied to builders', cabinet, and furniture hardware, lighting fixtures, belt buckles, and novelties. Brass deposits of specific composition have been used as a means of bonding rubber to metal[24]. Brass has also been electrodeposited on steel cartridge cases[25, 26].

Typical copper-zinc alloy plating baths are given in Table 38-3. Bath No. 1 is a conventional decorative brass bath[27]. The Rochelle salt brass bath No. 2[23] operates over a wider range of temperature and current density. When used with periodic reversal of the current, it gives excellent bright deposits. Bath No. 3 was recommended by Coats[24] for depositing brass for bonding rubber to metal. Bath No. 4, developed by the author[23, 28], may be used for depositing both red and light bronze-colored deposits by varying the ammonia concentration and operating conditions.

TABLE 38-3. TYPICAL COPPER-ZINC ALLOY PLATING BATHS

Composition	1 Brass oz per gal.	2 Brass oz per gal.	3 Brass† oz per gal.	4 Bronze oz per gal.
CuCN	3.6	7.0	3.5	7.0
$Zn(CN)_2$	1.2	4.0	1.5	4.0
NaCN	7.5	12.0	6.0	12.0
Na_2CO_3	4.0	4.0	....	4.0
Rochelle salt	....	6.0	....	6.0
NH_4OH(28 per cent), ml per gal.	....	20—50*	....	0—15*
Analysis				
Free NaCN	2.3	1.0**	0.85	1.0**
Copper	2.5	5.0	2.5	5.0
Zinc	0.65	2.0	0.85	2.0
Solution ratio, Cu/Zn	80/20	70/30	75/25	70/30
Conditions				
pH, colorimetric	....	10.3—10.7	....	10.3—10.7
Temperature, °F	95—120	110—140	95—120	110—140
Current density, amp per sq ft	5	5—35	5.0	5—35
Cathode efficiency‡, per cent	....	90—70	....	90—70

† For rubber adhesion.
* Added as required to adjust color.
** 0.5—1.5 oz per gal. may be used.
‡ Efficiency depends largely on temperature and current density used.

The ratio of copper to zinc in these alloy plating baths, the concentration of ammonia and free cyanide, the pH, temperature, and current density must all be controlled to obtain uniform results. The anode composition for brass or "bronze" plating should be approximately the same as the composition of the deposit. Only high-purity cast or rolled anodes should be used. The anode area should be about twice the cathode area.

Other copper alloys have been plated. A copper-cadmium bronze bath has been recommended for bronze-colored deposits as being easy to control[29]. Copper-tin alloy baths have been used for plating tin bronze and speculum[30, 31] deposits.

A low-copper high-zinc white brass[32] and a copper-zinc-tin white alloy[33] have also been electrodeposited. White brass containing copper as low as 1 per cent can be buffed and successfully chromium plated.

Materials of construction for any of the alloy processes mentioned are all the same. Steel may be used. Tank linings of rubber or plastic are satisfactory and preferred. Lead cannot be used.

Chemical Coloring

Chemical coloring of metals, particularly copper, brass or (copper-zinc) bronze coatings, to give various antique or oxidized finishes is quite common. It is necessary to protect these finishes with a clear organic coating. Information on chemical coloring may be found in references 34, 35, and 36.

In discussing metal coloring, Hogaboom[36] states: "The application of colors to metals is older than is generally realized. It was in a high state of development as early as several centuries B.C. The early alchemist was a colorer of metals . . .

"Regardless of how minutely a process of coloring metals is written, it is most difficult to visualize the exact resulting color. The weakness of all formulas lies in that very fact. Another contributing factor is the composition and even the physical structure of the metal upon which a color is to be applied.

"To attempt to describe even a part of the methods to produce colors on metals would require a symposium of several days; and then, if all the formulas suggested for even one color were followed and specimens made, the assembly of them in all probability would resemble grandmother's crazy quilt."

These words might be said with equal truth about coloring only copper and its alloys. As Hogaboom[36] further points out, copper lends itself to an unlimited variety of finishes. Probably the widest range of colors is obtained through the use of soluble sulfides, a mixture of sulfides with other chemicals, or by producing various effects by a subsequent treatment. The sulfide finishes are popularly called oxidized finishes. The color is frequently removed from selected areas or "high lights" to produce combination color effects.

A "verde" or "verde antique" finish, to imitate the corroded finish on ancient bronzes, may be produced on copper or its alloys, especially brass, from a large number of formulas and procedures.

Processes for producing black finishes on copper and its alloys include black nickel[37], "moly" black[38], and cupric oxide black[39].

ELECTROLYTIC COLORING

A novel coloring process sold under the trade mark "Electrocolor" in which cuprous oxide is deposited at the cathode from a proprietary alkaline divalent copper bath was first reported by Stareck[40]. The production of various spectral colors depends upon the thickness of the deposit, and with the bath composition, temperature, and current density controlled, the color then becomes a function of time. In applying the process to a copper or brass basis metal the desired bright or matte surface is first produced by conventional means, after which the parts are cleaned and the "Electrocolor" is applied. A copper strike must first be applied over a steel or zinc basis metal. After coloring, the parts are rinsed, dried, and then given a clear lacquer coating for protection.

"Patternplate," a modification of the above process, is produced from the same bath by continued electrodeposition and reduction of the cuprous oxide to form spangle, crystal, crackle, and dendrite or fern-like patterns. The parts are usually plated subsequently with some other metal, such as silver or nickel, and then lacquered. The pattern is visible through the subsequent plated coating. Many combinations of colors, patterns, and plated finishes are possible.

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Chapter 39

The Simpler Inorganic Compounds of Copper

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The Oxidation States of Copper

Copper is chemically related to the other elements of group IB of the periodic table—silver and gold. Elements of this subgroup have only one *s* electron in the outermost level, but the configuration of the remaining electrons is not of the noble-gas type, and oxidation states higher than +1 are possible by removal of one or two *d* electrons. Copper forms compounds in which its oxidation state is +1 (cuprous), +2 (cupric), and +3 (a few unstable compounds). The standard oxidation-reduction potentials of the oxidation states of copper are:[43]

$$\begin{aligned} Cu^0 &\rightleftharpoons Cu^+ + e^-, && -0.52 \text{ volt} \\ Cu^+ &\rightleftharpoons Cu^{++} + e^-, && -0.15 \text{ volt} \\ Cu^{++} &\rightleftharpoons Cu^{+++} + e^-, &> &-1.8 \text{ volts} \end{aligned}$$

The Nature of Monovalent Copper

Many of the simple cuprous compounds are insoluble in water, and resemble the corresponding compounds of silver and gold. In water, the soluble cuprous compounds are unstable and disproportionate into metallic copper and the cupric ion. This means that the equilibrium, $2Cu^+ \rightleftharpoons Cu^0 + Cu^{++}$, is spontaneous ($E^0$, +0.37 volt). However, many of the cuprous compounds (oxide, sulfide, halides) are so insoluble that the concentration of cuprous ions never reaches the very low limit set by the above equilibrium. Further, the cuprous ion forms many stable complex ions, and with many of these the above equilibrium is reversed. Thus the preparation of cuprous compounds from metallic copper and a cupric salt is possible.

The stability of the cuprous over the cupric state is increased at high temperature. Cupric oxide and sulfide are transformed to the corresponding cuprous compound at 900°C (1650°F) and at a red heat, respectively. This is illustrated by the sole presence of univalent copper in many igneous minerals. The halides undergo similar transformation, the decomposition temperature decreasing with increasing atomic weight of the halogen until for the iodide only the cuprous compound can be prepared[103].

The nature of copper in the univalent state has received attention because of the association of the halides in the vapor state. From potentiometric and solubility studies[90], it appears that the ionic species is Cu^+ and that the representation Cu_2^{++}, appearing in the older literature, is not justified[103].

The physical properties of some important cuprous compounds are given in Table 39-1 and important uses for cuprous compounds are described in a later section of this chapter.

The Simpler Cuprous Compounds

Cuprous acetate, $CuOCOH_3$, is formed as a sublimate when cupric acetate is heated *in vacuo* above 220°C (428°F). It is a colorless crystalline compound and is hydrolyzed rapidly by water to cupric oxide[119].

Cuprous acetylide. When acetylene or a derivative containing the $C \equiv C-H$ group is passed into an ammoniacal solution of a cuprous salt, a precipitate of a cuprous compound results. The reaction has been used for the estimation of copper[122]. With acetylene, the product has the composition $Cu_2C_2.H_2O$ when dried over calcium chloride in the cold[123]. When dried similarly at 80 to 100°C (176 to 212°F) or in a stream of carbon dioxide, the red to brown cuprous acetylide, Cu_2C_2, is formed[123, 63]. The compound is explosive when dry or when placed in contact with nitric acid, sulfuric acid, or halogens[124, 63]. It has been studied as an ingredient of fuse compositions.

Copper borohydride, $CuBH_4$, is quantitatively formed by the action of an ethereal solution of lithium borohydrate upon a suspension of cuprous chloride in tetrahydrofuran at −20°C. The compound decomposes at 0°C to various products, including cuprous hydride[80, 118].

Cuprous bromide, CuBr, forms as a white crystalline powder, but in a moist condition or when exposed to strong sunlight, it gradually becomes green or dark blue, respectively. The molten salt is gray-brown or green-brown in color. The properties and reactions[63] of cuprous bromide resemble those of chloride. The vapor pressure in the range 910 to 1100°C (1670 to 2010°F) indicates association with formation of the dimer Cu_2Br_2[38, 78], and/or the trimer[13]. The compound dissolves in solutions of various alkali metal halides, and in aqueous ammonia with the formation of complexes. Cuprous bromide is prepared by the reduction of soluble cupric salts by sulfur dioxide or by metallic copper. It can also be prepared by the interaction of cuprous chloride with hydrobromic acid[25].

TABLE 39-1. PHYSICAL PROPERTIES OF SOME COPPER COMPOUNDS

Formula	Formula Weight	Color and Crystalline Form	Specific Gravity
CuBr	143.46	tetra., cu., wh.	4.72
CuCl	99.00	cub., wh.	3.53
CuCN	89.56	monocl., wh.	2.9
CuH	64.55	br.	5.7 (6.4)
CuI	190.45	cub., wh. (min., r.-br.)	5.59-5.62
Cu_3N	204.63	dk. gr. powd.	
Cu_2O	143.08	cub., r. (rarely br.-blk.)	5.85-6.15
Cu_3P	221.60	gray-blk.	6.4-6.8
Cu_4Si	282.25	wh., met.	7.53
Cu_2S	159.15	rhomb., blk. (cub., blk.)	5.7 (5.8)
$Cu_2SO_3 \cdot H_2O$	225.16	pr., r. (hex., wh.)	4.46 (3.83)
CuSCN	121.62	wh. to yel. powd.	2.85
Cu_5As_2	467.52	oct., bl.	7.56
$CuBr_2$	223.37	monocl., blk., del.	
$CuCO_3 \cdot Cu(OH)_2$	221.11	monocl., dk. gr.	3.9-4.0
$2CuCO_3 \cdot Cu(OH)_2$	344.66	monocl., bl.	3.8
$Cu(ClO_3)_2 \cdot 6H_2O$	338.55	cub., gr., del.	
$CuCl_2$	134.45	br.-yel. powd.	3.05
$CuCl_2 \cdot 2H_2O$	170.49	rhomb., gr. to bl.-gr., del.	2.39
$CuF_2 \cdot 2H_2O$	137.57	monocl., bl.	2.9
$Cu(IO_3)_2$	413.36	monocl., gr.	5.24
$Cu(IO_3)_2 \cdot H_2O$	431.38	tri., bl.	4.58 (4.87?)
$Cu(NO_3) \cdot 3H_2O$	241.60	rhomb. pl., bl., del.	2.05
$Cu(NO_3)_2 \cdot 6H_2O$	295.65	pr., bl., del.	2.07
CuO	79.54	blk., tetra., cub. (or tri.)	6.40 (6.45)
$Cu(OH)_2$	97.56	bl., hydrogel or cryst.	3.37
$CuSO_4$	159.61	rhomb., wh.-gr.	3.60
$CuSO_4 \cdot 5H_2O$	249.69	tri., bl.	2.28
$CuSO_4 \cdot 4NH_3 \cdot H_2O$	245.75	rhomb., bl.	1.81
CuS	95.61	hex. or monocl., bl.	4.6
$Cu(SCN)_2$	179.71	blk.	

Copper reacts vigorously with bromine vapor at a dark red heat to form a mixture of cuprous and cupric bromides. With an excess of bromine, only cupric bromide is formed.

Cuprous carbonate has not been isolated as the normal carbonate, Cu_2CO_3, although there is evidence for its existence.

Cuprous chloride (*nantokite*), CuCl, forms as a white, crystalline powder that changes in color from yellow through green and violet to a blue-black on exposure to light and moist air. The vapor of cuprous chloride appears to contain the trimer Cu_3Cl_3, some CuCl, but contrary

TABLE 39-1. PHYSICAL PROPERTIES OF SOME COPPER COMPOUNDS (Cont'd)

Melting Point (°C)	Water Solubility	Other Solubilities	Abbreviations
504	sl. s. cold; d. hot	s. HBr, HCl, HNO_3, NH_4OH; i. HOAc	ac., acetate al., ethyl alcohol
422 (432)	sl. s. cold	s. HCl, NH_4OH, al.; i. H_2SO_4, dil. HNO_3	aq., aqueous bl., blue
474	i.	s. HCl, NH_4OH, KCN	blk., black
d. 105-130	i.		br., brown
605 (588)	i.	s. NH_4OH, KCl, KCN	conc., concentrated
d. 300	d. cold	d. acids	cryst., crystals
1235	i.	s. HCl, NH_4Cl, NH_4OH; sl. s. HNO_3; i. al.	cu., cubic d., decomposes
d.	i.	s. HNO_3; i. HCl	del., deliquescent
850	i.	s. HNO_3; i. HCl	dil., dilute
1107-1127	i.	s. HNO_3, NH_4OH; i. HOAc	dk., dark et., ether
d.	(see text)	(see text)	ext., extremely
d. 300-400	i. cold	s. NH_4OH, et., conc. acids; i. dil. acids, al.	gr., green hex., hexagonal
d.	i. H_2O	s. NH_4OH, acids	i., insoluble
498	v. s. cold	s. al., acetone, pyr., NH_4OH	liq., liquid met., metallic
d. 200	i. cold; d. hot	s. KCN, dil. acids, NH_4OH	meth., methanol min., mineral
d. 220	i. cold; d. hot	s. NH_4OH, hot aq. $NaHCO_3$	monocl., monoclinic oct., octahedral
65	v. s. cold	s. al., HOAc	pl., plates
498 (?)	s.	s. al., meth., acetone	powd., powder
110 ($-2H_2O$)	v. s. cold	s. al., NH_4Cl; sl. s. et.	pr., prismatic
	sl. s. cold; i. hot	s. al., acids, pyr.	pyr., pyridine
d.	sl. s. cold; i. hot	s. dil. HNO_3, H_2SO_4	r., red
240 ($-H_2O$)	sl. s. cold	s. dil. H_2SO_4	rhomb., rhombic
114.5	ext. s. cold	v. s. al.	s., soluble
26.4 ($-3H_2O$)	ext. s. cold	s. al.	sl., slightly
1026 d.	i.	s. acids, NH_4Cl, KCN	tetra., tetrahedral
d. ($-H_2O$)	i. cold; d. hot	s. acids, NH_4OH, al.	tri., triclinic
d. 200	s. cold; v. s. hot	s. meth.; i. al.	v., very
110 ($-4H_2O$)	s. cold; v. s. hot	s. meth.; al. HOAc	wh., white
150 d.	s. cold; d. hot	i. al.	yel., yellow
d.	i.	s. hot, HNO_3, NH_4OH; KCN; i. al.	
d.	v. sl. s.	s. NH_4OH; i. al.	

to earlier conclusions[12, 71] no dimer Cu_2Cl_2[13]. Cuprous chloride is readily soluble in hydrochloric acid and solutions of alkali metal halides through formation of complex ions such as $[CuCl_2]^{-1}$ and $[CuCl_3]^{-2}$, and in aqueous ammonia through formation of colorless complex ions such as $[Cu(NH_3)_2]^{+1}$. Cuprous chloride is hydrolyzed quickly by hot water to red, hydrated cuprous oxide. Its solution in hydrochloric acid is oxidized by air, finally depositing basic cupric chloride.

Cuprous chloride is formed by heating cupric chloride (or sulfate) with hydrochloric acid (sodium chloride may be added) and copper turnings, followed by dilution with water[51]. The reaction may be carried to completion by addition of sulfur dioxide. A convenient preparation is the reduction of cupric chloride with sulfur dioxide or with other reducing agents[37, 58]. Cuprous chloride in aqueous ammonia or concentrated hydrochloric acid is an effective absorbent for oxygen and carbon monoxide. With oxygen, amine or chloro complexes are formed; with carbon monoxide, an unstable compound forms[39] corresponding under certain conditions to $CuCl.CO.2H_2O$[10]. Solid anhydrous cuprous chloride reacts with carbon monoxide at high pressures, possibly forming the compound $CuCl.CO$[116].

Cuprous cyanide, $CuCN$, forms as colorless crystals, but is often colored by the presence of trace impurities (iron). Commercial material is often a creamy white powder. Like the iodide, it is formed by the internal oxidation-reduction of the corresponding cupric salt. Cupric cyanide, which is first precipitated by the action of potassium cyanide on soluble cupric salts, soon breaks up into cuprous cyanide and cyanogen. Cuprous cyanide can be made in almost quantitative yield from cupric sulfate, potassium cyanide, and sodium bisulfite[6]. It is decomposed by nitric acid and by boiling dilute hydrochloric acid to form cuprous chloride and hydrocyanic acid. It is soluble in aqueous ammonia and solutions of some ammonium salts.

Cuprous cyanide combines with excess soluble cyanides to form cuprocyanides (*i.e.*, cyanocuprates[I]). Solid salts of three types have been obtained: $M[Cu(CN)_2]$, $M_2[Cu(CN)_3]$, and $M_3[Cu(CN)_4]$[63]. E. M. F. measurements of solutions have shown $[Cu(CN)_4]^{-3}$ to be the principal ion species present; however, some $[Cu(CN)_3]^{-2}$ is also present, especially at higher dilutions[63, 100]. The free (hydrated) cuprous ion in a decinormal solution of one of these cuprocyanides may be less than one atom in 33,000 liters. The tendency of copper to form cyanide complexes is so great that copper will dissolve slowly in concentrated potassium cyanide solution, hydrogen being evolved.

Cuprous cyanide is manufactured by two methods. In the older method aqueous solutions of sodium hydroxide and sodium bisulfite are added simultaneously to a cupric sulfate solution. A solution of sodium cyanide is then added and the cuprous cyanide is removed, washed, and air-dried. In the newer method cupric chloride is reduced with copper scrap in a hot sodium chloride solution, reduction being completed with sulfur dioxide. The resulting cuprous solution is treated with sodium cyanide solution, and the cuprous cyanide precipitated is removed, washed free of chloride, and dried[53]. The product by the second method is of high purity.

Cuprous ferrocyanide, $Cu_4Fe(CN)_6$, is formed by treatment of cuprous chloride in concentrated hydrochloric acid with potassium ferrocyanide.

The white product is contaminated with potassium ion, is soluble in aqueous ammonia, and is easily oxidized in the air[55].

Cuprous fluoborate is formed in toluene solution by treatment of a stoichiometric mixture of copper metal and cupric fluoride with boron trifluoride[117]. On addition of dilute sulfuric acid to the toluene filtrate, the compound disproportionates to metallic copper and a green cupric solution[117].

Cuprous fluoride, CuF, probably does not exist in the pure state. The literature concerning it has been reviewed by Emeleus[20] and by Sidgwick[63] (see also *cupric fluoride*).

Cuprous hydride. Wurtz in 1844 found that on warming cupric sulfate with hypophosphorus acid, H_3PO_2, a brown solid forms, presumably cuprous hydride (CuH). On heating, the product evolves hydrogen. It is insoluble and cannot be purified. Hüttig and Brodkorb[35] found that the product does contain cuprous hydride, but that it is mixed with copper, copper oxide, and water. This preparation has also been reviewed by Wiberg and Henle[80, 118] and by Hurd[36]. Warf and Feitknecht[76] have reported x-ray data for the product and for the corresponding cuprous deuteride, CuD. Cuprous hydride prepared by the reduction of cupric salts is oxidized slowly by air in the cold, and on heating evolves hydrogen, at first slowly and then rapidly at 110 to 120°C[35]. It is also known to decompose explosively when dried over dehydrating agents[55, 64]. Wiberg and Henle[80, 118] have reported that cuprous iodide and lithium aluminum hydride react in organic solvents to form a cuprous hydride, CuH, that is soluble in pyridine with a dark red color, that shows reducing properties, and that is identical in color, composition, and decomposition temperature with the earlier preparation obtained from aqueous solution. However, it is distinguished from the latter by being water-free and by reducing benzoyl chloride to benzaldehyde. The cuprous hydride (from hypophosphite) prepared by Sieverts and Gotta[64] had a molar heat of formation of −5.12 kilocalories, which points to its being metallic rather than salt-like in character[64, 103]. The spectrum of copper vapor in hydrogen indicates the presence of a copper hydride with a molar heat of dissociation of about 65 kilocalories[24].

Cuprous iodide, CuI, is the only iodide of copper known in pure form. It is found in the mineral *marshite*. The pure compound is a white to pale yellow crystalline powder and is less sensitive to light than the corresponding bromide and chloride. On heating, it turns a dark red, then brown, and finally black; on cooling, the original color returns. Vapor-pressure studies of the gaseous cuprous iodide indicate the presence of polymeric molecules[13]. Cuprous iodide differs from the other cuprous halides in being formed directly by warming a solution of a cupric salt with potassium iodide. One-half of the iodine is precipitated as cuprous iodide and half is liberated as free iodine. This reaction has been used for the quantitative determination of copper. In the presence of ferrous sulfate or sulfurous acid, all of the iodine is precipitated as cuprous iodide. Cuprous iodide is also formed by the interaction of free iodine with hot, finely divided copper.

Cuprous nitrate. The isolation of pure cuprous nitrate, $CuNO_3$, is doubtful. By placing a solution of cupric nitrate in liquid ammonia in contact with copper foil, crystals of a cuprous ammino-nitrate, $CuNO_3 \cdot 2NH_3$, are obtained[21, 65]. On evaporation of the ammonia, cupric nitrate is reported to be formed[51]; however, the impure product oxidizes rapidly in air.

Cuprous nitride, Cu_3N, is produced by passing ammonia over anhydrous cupric fluoride at 280°C and also by heating copper to redness in ammonia[41]. It is a dark green powder that is stable in air when cold. It decomposes into its elements on heating *in vacuo* at 450°C (840°F). It is dissolved by acids with the formation of cupric salts and metallic copper[40]. Presumably, the same nitride is formed by treating copper nitrate in liquid ammonia with potassium amide, KNH_2, and heating the resulting green precipitate ($CuNH_2$, possibly) to 160°C (320°F) *in vacuo*[27].

Cuprous nitrite, $CuNO_2$, is unknown.

Cuprous oxide, Cu_2O, occurs as the mineral *cuprite*. Cuprous and cupric oxides are the two principal oxides of copper. Oxides assigned the formulas CuO_2, Cu_3O, and Cu_4O have been reported. Some of these oxides are probably solid solutions of copper in cuprous oxide. Cuprous oxide has been shown by its crystal structure to be a covalent compound[56]. Cuprous oxide forms as dark or carmine red crystals or microcrystalline powder. The color of the compound varies with the method of preparation and with particle size, and has been described as yellow, orange, red, and dark brown. X-ray studies[11, 68] prove that specimens of varying color do not differ in crystal structure. Earlier workers had supposed that two forms of the oxide exist, yellow and brown, or that the red form is the true oxide and the yellow the hydroxide[63]. The pale yellow color of the precipitate formed from alkali and cuprous chloride suggests that it may be a hydroxide, but no product of this composition has been isolated[63].

The manufacture of cuprous oxide proceeds usually either by furnace or electrolytic oxidation. In the furnace process, either cuprous or cupric oxide or mixtures of the two are formed, depending upon the temperature, the rate of heating, and the rate of cooling. Cuprous oxide is produced by bringing the charge to such a temperature that the decomposition pressure of cupric oxide is greater than the partial pressure of oxygen in the atmosphere. The charge is allowed to cool in an inert atmosphere or is quenched rapidly. The furnace may be charged with various scale products from the anodes of copper refineries and various mixed copper oxides obtained as by-products in the refining and fabrication of copper[5, 73]. Cuprous oxide has also been manufactured as a floating slag by blowing air through molten refined copper in a converter. The molten oxide is cast, crushed, and pulverized.

In the electrolytic process, cuprous oxide is plated from an alkaline sodium solution using an anode of refined copper and a cathode of sheet copper. The particle size may be controlled by adjustment of temperature, pH, contact time of the oxide with the solution, and current density[1, 73]. For use in antifouling paints, the bright red grade is preferred, and for fungicidal use, the finer, yellow sizes. Most of the cuprous oxide for antifouling purposes is produced at present by the furnace method because it is difficult to remove traces of salts from the electrolytic product that cause it to be hygroscopic and therefore easily oxidized. Miscellaneous methods for preparing cuprous oxide include heating cuprous chloride and sodium carbonate in a covered vessel and separating the oxide by lixiviation; reducing alkaline solutions of cupric salts (*e.g.*, Fehling's solution); heating a mixture of cupric oxide and copper filings in the proper proportions in a covered vessel; and heating cupric oxide in a stream of sulfur dioxide and treating the product with water to remove the sulfate[82].

Cuprous phosphide, Cu_3P, is present in the alloy known as phosphor-copper, which contains from 9 to 15 per cent phosphorus. This compound is produced by the interaction of copper and phosphorus[82] or by the electrolysis of a fused mixture of alkali metal phosphates and copper compounds[4, 16]. By the latter method, the formation of the compound Cu_2P has also been reported[16]. Alloys containing more than 15 per cent phosphorus must be prepared in closed containers because of the volatility of the phosphorus. **Cuprous silicide,** Cu_4Si, is produced when copper and silicon are heated in an electric furnace. It is attacked by chlorine and *aqua regia.*

Cuprous sulfate, Cu_2SO_4, is obtained as a gray-white powder by the action of dry dimethyl or diethyl sulfate on dry powdered cuprous oxide[44, 61]. It is stable in the absence of moisture. It is soluble in concentrated hydrochloric acid, ammonia, and glacial acetic acid, giving an intensely violet solution with the last solvent. A cuprous basic sulfate (oxysulfate) has been prepared by the electrolysis of an acidified cupric sulfate solution[28].

Cuprous sulfide, Cu_2S, occurs as the mineral *chalcocite* or *copper glance,* an important copper ore. The mineral is in the form of rhombic crystals and is colored gray, black, blue, green, or violet. The synthetically prepared rhombic form is generally black or blue-black. A black octahedral cubic crystalline form has also been prepared. Cuprous sulfide dissolves in cold nitric acid to form cupric nitrate and sulfide, and in hot nitric acid to form cupric nitrate, sulfur, and other products. The compound is decomposed by concentrated sulfuric acid to cupric sulfide and sulfate with the liberation of sulfur dioxide. On heating in the absence of air, it forms metallic copper and cupric sulfide; in the presence of air it forms cupric oxide and sulfate as well as sulfur dioxide. Cuprous sulfide is reduced slowly by hydrogen at a red heat, but is largely unaffected by carbon and carbon monoxide. It may be prepared by heating a mixture of copper and sulfur, by subjecting the mixture to high pressures at room temperature[54], and also by interacting metallic copper and certain sulfides (magnesium, aluminum, etc.).

Cuprous sulfite hydrate, $Cu_2SO_3.H_2O$, exists in both a red prismatic and a white hexagonal crystalline form. The red form is insoluble in water and alcohol, but soluble in ammonium hydroxide and hydrochloric acid. The white form is slightly soluble in cold water, soluble in ammonium hydroxide, hydrochloric acid and alkali, but insoluble in alcohol and ether. The white form changes to the red by the action of sulfur dioxide[73]. The compound is obtained by passing sulfur dioxide into a hot solution of cuprous acetate in acetic acid[73]. It forms double salts with alkali metal sulfites.

Cuprous thiocyanate (cuprous sulfocyanide), CuSCN, is formed as a white to yellow amorphous precipitate when a soluble thiocyanate is treated with a solution of a cupric salt in the presence of a reducing agent such as sulfur dioxide. The manufacture of a high-purity grade of this compound has been described[18]. The compound is insoluble in water and alcohol, and is stable in air. It dissolves in solutions of soluble thiocyanates producing complexes. The literature on cuprous thiocyanate has been summarized by Williams[81] and Beilstein[8].

The Nature of Divalent Copper

Cupric compounds correspond somewhat to the divalent compounds of nickel, cobalt, and iron (*i.e.,* the transitional elements preceding copper in the periodic table), and of zinc (the element following next). The hydrated sulfates of these metals are isomorphous with cupric sulfate and form hydrated double compounds with it. The cupric ion Cu^{+2} is paramagnetic and is strongly colored (presence of incomplete group of 17 electrons). In dilute solution cupric salts of strong acids show strong light absorption, especially in the infrared portion of the spectrum, due to the presence of hydrated cupric ion, possibly $Cu(OH)_4^{+2}$. At higher concentrations, or in the presence of the corresponding alkali metal salt of the strong acid, the color changes from blue-green to green or brown due to the formation of a differently colored complex ion. Hydrated cupric salts are generally blue to green (if the anion is colorless), but the anhydrous salts vary in color from white (CuF_2) to black ($CuBr_2$). The cupric salts are generally more soluble than the corresponding cuprous compound, and cupric salts of strong acids are slightly acid by hydrolysis. A large number of basic cupric salts are known; however, many so-called basic cupric salts may be only colloidal mixtures[63].

The physical properties of some important cupric compounds are given in Table 39-1 on page 786, and their preparation and chemical reactions are described below. Important uses for cupric compounds are described in a later section of this chapter.

The Simpler Cupric Compounds

Cupric acetate (crystallized or neutralized verdigis), $Cu(C_2H_3O_2)_2.H_2O$, is manufactured usually by the action of acetic acid on cupric oxide or carbonate. It is an intermediate in the manufacture of Paris green (*q.v.*). The basic cupric acetates (copper subacetate), $2Cu(C_2H_3O_2)_2.CuO.H_2O$ (common or green verdigris) and $Cu(C_2H_3O_2)_2.CuO.H_2O$ (blue or French verdigris), are also commercially available. The basic acetates are usually prepared by the action of acetic acid and air on copper scrap.

Cupric acetoarsenites. *Paris green* (Schweinfurt green, Emerald green) is a complex of copper metaarsenite and cupric acetate with the approximate composition $(CH_3COO)_2Cu.3Cu(AsO_2)_2$. This brilliant green complex is usually manufactured by the interaction of a cupric sulfate or chloride solution with a solution of sodium carbonate and arsenious oxide. The precipitate of cupric arsenite is allowed to stand, and cold dilute acetic acid is then added. The arsenite is converted to the acetoarsenite with the evolution of carbon dioxide. The product is washed, filtered, and dried. In another process basic cupric acetate is first formed. Paris green is readily broken down in the presence of water[29, 30].

Cupric arsenate. The preparation of the normal cupric arsenate is in doubt[49]; however, a large number of basic and acidic arsenates are known. The literature is reviewed by Mellor[51], and by Mas[49], and by Frear[30].

Cupric arsenite (*Scheele's green* or *Swedish green*) is a compound of variable composition prepared by the interaction of a cupric salt with a solution of sodium carbonate and arsenious oxide. The greater the excess of alkali used, the higher the copper content. The shade is influenced by the amount of arsenious oxide used and ranges from pale to dark green. The literature on cupric arsenite and related arsenical pigments is reviewed by Mellor[51] and Ullmann[72].

Cupric borate. By the interaction of a solution of borax with cupric sulfate, blue to blue-green precipitates of varying composition can be obtained. Material corresponding in analysis to the true cupric borate, $Cu(BO_2)_2$, is obtained by melting cupric oxide with ten times the theoretical amount of boric acid anhydride. The lower layer after solidification is treated with water and the pure crystalline material remains undissolved.

Cupric bromide, $CuBr_2$, forms as black, deliquescent crystals. An olive green tetrahydrate (long, monoclinic needles, transition at about 18°C) is known, but no other hydrate[15]. A concentrated solution of cupric bromide in water is dark brown in color, but on dilution changes first to green and finally to blue. This has been explained by the progressive dissociation of the complex ion $[CuBr_4]^{-2}$ into the hydrated cupric ion and bromide. By addition of excess potassium bromide, the color of a solution of cupric bromide becomes purple-red. The crystal structure of the anhydrous salt has been investigated[33]. Cupric bromide is formed by the interaction of metallic copper and bromine water or by the action of hydrobromic acid on cupric oxide. At a dark red heat in the presence of excess bromine vapor, metallic copper reacts to form the anhydrous salt.

Cupric bromate is best known as the blue-green hexahydrate, $Cu(BrO_3)_2.6H_2O$, which is soluble in aqueous ammonia and slightly soluble in cold water.

Cupric carbonate. The normal cupric carbonate, $CuCO_3$, has not been isolated, but numerous basic carbonates have been reported as well as double salts with ammonium and other carbonates. Several basic carbonates occur naturally, the best known of which are *malachite*, $CuCO_3.Cu(OH)_2$, and *azurite*, or *chessylite*, $2CuCO_3.Cu(OH)_2$. Commercial basic cupric carbonate is in the form of a green to blue amorphous powder or dark green monoclinic crystals. It is often manufactured by the addition of sodium carbonate or other soluble carbonate to cold solutions of cupric sulfate or nitrate. The degree of basicity of the carbonate formed depends on the conditions of precipitation. The literature concerning the preparation of basic copper carbonates for fungicidal use has been reviewed by Frear[30].

Cupric chlorate, $Cu(ClO_3)_2$, is known in the form of the green deliquescent tetrahydrate[93, 101] and possibly as the hexahydrate[115], which are very soluble in water. A blue-green basic cupric chlorate, slightly soluble in water, of approximate composition $Cu(ClO_3)_2.3Cu(OH)_2$, and the ammino-salts $Cu(ClO_3)_2.6NH_3$ and $Cu(ClO_3)_2.4NH_3$ have also been prepared.

Cupric chloride, $CuCl_2$, in an anhydrous condition is a brown-yellow deliquescent, microcrystalline powder. Both anhydrous crystalline cupric chloride and bromide have chain structures involving halogen bridges and are largely covalent[33]. Cupric chloride forms a series of hydrates containing 4, 3, 2, and 1 molecules of water. The ordinary salt crystallized from aqueous solutions is the dihydrate, which has a blue color but when moist appears green, because the crystals are covered with a thin film of the brown-colored saturated solution. The concentrated solution is dark brown, but on progressive dilution becomes green and then pale blue. The addition of an alkali metal chloride or a rise in temperature has an effect on the color similar to an increase in concentration[63, 102, 108]. Anhydrous cupric chloride is formed by heating copper and an excess of chlorine, by heating the dihydrate in a stream of hydrogen chloride gas, or by dehydrating the dihydrate over sulfuric acid. The dihydrate is obtained by treating cupric oxide, hydroxide, or basic carbonate with hydrochloric acid, and concentrating the solution. Depending on the concentration of sulfuric acid added to a solution of cupric chloride, the anhydrous form or the dihydrate crystallizes out. Basic cupric chlorides (copper oxychloride) are formed when cupric chloride is exposed to air. The basic chlorides are variable in composition, and some occur naturally. They may be manufactured by electrolysis of brine at a copper anode, and by the controlled neutralization of cupric oxide with hydrochloric acid in water. A process has also been described[60] involving solution of a copper mineral in sulfuric acid, addition of sodium chloride, reduction with sulfur dioxide, and oxidation of the cuprous chloride isolated with air. The recovered sulfuric acid liquor is used to dissolve more of the mineral.

Cupric chromate and chromite. A neutral cupric chromate, $CuCrO_4$, is obtained through precipitation of a copper sulfate solution with potassium chromate as a yellow-brown precipitate. Various basic chromates are better known. Cupric ammonium chromate is prepared by mixing a water solution of a cupric salt, a chromate, and ammonium hydroxide. On heating this salt to a suitable temperature (150 to 250°C), it decomposes to a mixture of cupric oxide and cupric chromite, $CuCr_2O_4$. X-ray diffraction study of this mixture and its intermediates has been reported[69]. This mixture has found application in recent years as a selective hydrogenation catalyst[3]. The catalytic activity seems dependent on the cupric oxide-cupric chromite ratio[2].

Cupric cyanide, $Cu(CN)_2$, is an unstable substance formed as a yellow to brown precipitate when potassium cyanide is added to a cupric salt solution. It rapidly changes to $Cu(CN)_2.2CuCN.5H_2O$ with evolution of cyanogen, and on warming it is converted to cuprous cyanide (*q.v.*)[81].

Cupric ferricyanide, $Cu_3[Fe(CN)_6]_2.14H_2O$, forms as a yellow-green precipitate by the interaction of cupric ion and soluble ferricyanides in solution. It is soluble in aqueous ammonia and ammonium carbonate, but is insoluble in solutions of other ammonium salts, in water, and in dilute hydrochloric acid. The structure of the compound has been studied by Gaur and Bhattacharya[94].

Cupric ferrocyanide. The precipitation of cupric ion by potassium ferrocyanide solution leads to potassium-contaminated precipitates. Excess cupric ion or high acidity is required to obtain the simple, red-brown cupric ferrocyanide $Cu_2Fe(CN)_6.xH_2O$[85]. It is soluble in aqueous ammonia, but insoluble in water, dilute acids, and ammonium salts. Numerous double salts are known, including a calcium salt formulated by some workers as $Ca[CuFe(CN)_6]$[85].

Cupric fluoride, CuF_2, is a white crystalline solid. On exposure to moist air it is transformed to the dihydrate, $CuF_2.2H_2O$. The anhydrous compound can be made by passing hydrogen fluoride over copper oxide at 400°C or by heating fluorine and copper powder. It is also obtained when the hydrated fluoride is treated with ammonium fluoride and the product is heated at 260°C (500°F) in a stream of carbon dioxide to remove the excess ammonium salt. When the anhydrous cupric fluoride is heated to high temperature, there is apparently an equilibrium in the molten state between copper, cuprous fluoride, and cupric fluoride[59, 77]. The dihydrate is produced by evaporation of a solution of cupric oxide, hydroxide, or basic carbonate in hydrofluoric acid with sufficient excess acid to prevent precipitation of a basic fluoride, $CuF_2.Cu(OH)_2$. The normal fluoride decomposes slowly at room temperature to give the basic fluoride (oxyfluoride), $CuF_2.CuO$, and hydrogen fluoride. Wheeler and Haendler[125] have studied the thermal decomposition of cupric fluoride dihydrate. It undergoes a two-stage decomposition, forming $CuOHF.CuF_2$ at 132°C (270°F), followed by decomposition to the oxide and fluoride at 420°C (788°F). The related basic fluoride, CuOHF, also undergoes a two-stage decomposition, first forming $CuOHF.CuF_2$ at 345°C (653°F)[125]. The complex fluorides formed by the interaction of cupric fluoride with other metallic fluorides are reviewed by Emeleus[20].

Cupric iodate precipitates as the pale-blue crystalline monohydrate, $Cu(IO_3)_2.H_2O$, by the addition of excess potassium iodate to a solution of cupric nitrate. The anhydrous salt is formed by heating the hydrate at 240 to 250°C (460 to 480°F)[51].

Cupric iodide, CuI_2, is unstable. It breaks up rapidly into cuprous iodide and iodine. The isolation of higher iodides (CuI_4, CuI_6, and CuI_8) has been reported during the attempted preparation of cupric iodide.

Cupric nitrate, $Cu(NO_3)_2$, forms hydrates with 9, 6, and 3 molecules of water. From a solution of metallic copper or cupric oxide in very dilute nitric acid at temperatures above 26.4°C, the trihydrate crystallizes, and at lower temperatures the hexahydrate. It is reported that the anhydrous salt may be obtained by the action of nitrogen pentoxide on the hydrated salt. A basic cupric nitrate (green powder or blue-green crystals) is formed by heating the cupric nitrate hydrates or by boiling their solutions with copper, cupric oxide or hydroxide, or with alkali. Commercial basic cupric nitrate is usually obtained by the reaction of scrap copper with concentrated nitric acid, oxides of nitrogen being removed by blowing air through the solution.

Cupric nitride is unknown except as a solid solution with other nitrides; however, a black cupric azide, $Cu(N_3)_2$, and certain complex azides are known. **Cupric nitrite,** $Cu(NO_2)_2$, can be obtained as a blue to green precipitate of variable composition. The solid decomposes rapidly into cupric nitrate and nitric oxide, but solutions are moderately stable. A basic cupric nitrite, $Cu(NO_2)_2.3Cu(OH)_2$, is known as a green powder, stable in air.

Cupric oxide and **hydroxide.** Cupric oxide (copper monoxide, black oxide of copper), CuO, occurs as the minerals *tenorite* (triclinic) and *paramelaconite* (tetrahedral, cubic). Cupric oxide is a covalent compound[113] and is more acidic than cuprous oxide. Cupric oxide is manufactured either by furnace oxidation (see *cuprous oxide*) or by the indirect air oxidation of copper in the ammonia leaching process for the recovery of copper from ores. In the latter process, a solution of cuprous ammonium carbonate is boiled, evolving ammonia and carbon dioxide, and precipitating hydrated cupric oxide. Cupric hydroxide, $Cu(OH)_2$, precipitates from alkaline cupric salt solutions as a blue or blue-green hydrogel, which dries to friable lumps. On warming, the hydrogel turns black due to the formation of cupric oxide. However, the precipitated hydroxide can be dried carefully at 100°C to the composition $Cu(OH)_2$. Cupric hydroxide can also be prepared as blue crystals by placing an ammoniacal solution of the oxide over sulfuric acid in a desiccator. Cupric hydroxide is somewhat amphoteric, and dissolves when freshly prepared in alkalies to give a bright blue to violet solution containing hydroxocuprate ions, like $[Cu(OH)_4]^{-2}$. Cupric hydroxide is usually manufactured by the indirect air oxidation of metallic copper in the presence of ammoniacal solutions.

Cupric perchlorate hexahydrate, $Cu(ClO_4)_2.6H_2O$, is a very soluble salt (128.3 grams per 100 ml of water at 20°C)[91, 105]. It is freely soluble in methanol, ethanol, acetic acid and anhydride, and acetone. Over sulfuric acid it loses two molecules of water, but even over phosphorus pentoxide in the cold no further water is lost without decomposition. However, the existence of hydrates containing 7, 4, and 2 molecules of water has been reported[106, 111]. Basic salts such as $Cu(ClO_4)_2.6CuO.H_2O$ are known[87, 105], as are ammino salts[106] such as $Cu(ClO_4)_2.4NH_3.2H_2O$ and $Cu(ClO_4)_2.6NH_3$. The stability of cupric perchlorate in aqueous solution and its use as an analytical standard have been investigated[98].

Cupric periodate is known in the six-covalent form of the parent acid, $Cu_5(IO_6)_2.7H_2O$, which loses water to form the pentahydrate at 74°C *in vacuo*[63, 86]. A derivative of diparaperiodic acid, $Cu_4I_2O_{11}.H_2O$, has also been described[86].

Copper peroxide, CuO_2, is known only in a hydrated form produced by the action of hydrogen peroxide on a suspension of cupric hydroxide [97, 99, 104], on a solution of sodium copper carbonate[84], or on a solution of cupramine[112] at about 0°C. The yellow-brown to olive-green precipitate on washing with alcohol and ether and drying *in vacuo* approximates the composition $CuO_2.H_2O$. The product is a true peroxide as oxygen is liberated on warming and hydrogen peroxide is formed on addition of acid. By treatment of copper nitrate in anhydrous ethanol at −10°C with hydrogen peroxide in ether solution, unstable precipitates form having peroxidic activity[112]. After drying *in vacuo*, these precipitates approximate the composition $CuO.3CuO_2$ and $CuO.2CuO_2$, and are presumed to result from the decomposition of CuO_2 initially formed[112].

Cupric phosphate is known in nature in the form of various basic salts[51]. A study of the system P_2O_5-CuO-H_2O has been reported[96], casting doubt on earlier reports of the direct preparation of a hydrated cupric orthophosphate, $Cu_3(PO_4)_2.3H_2O$.

Cupric salts of carboxylic acids show a remarkable gradation in properties (solubility, color, etc.) as the homologous series is ascended. The literature is summarized by Sidgewick[53], and reviewed by Beilstein[8] under the individual acids.

Cupric silicate is found in nature in various hydrated forms[51]. Fusion of cuprous oxide and of cupric oxide with silica fails to reveal the formation of anhydrous copper silicates[88].

Cupric sulfate (copper sulfate, *hydrocyanite*) is known in the anhydrous form, $CuSO_4$, and forms hydrates containing 1, 3, and 5 molecules of water, and probably[70] 2 and 4. The anhydrous form is a gray-white to green-white crystalline or amorphous powder. The odd number of water molecules in the common hydrates has suggested that one is attached to the anion. However, the crystal structure of the pentahydrate is not as simple as this[7, 63].

The pentahydrate (blue vitriol, bluestone, *chalcanthite*), $CuSO_4.5H_2O$, crystallizes as large blue or ultramarine triclinic crystals from aqueous solution. When the pentahydrate is heated, it loses water to form the trihydrate at 30°C; this forms the monohydrate at 110°C, and the latter at 360 to 400°C (680 to 750°F) forms the anhydrous salt. On progressive heating above 560°C (1040°F), the anhydrous salt slowly loses oxygen and sulfur dioxide, forming first a gold-yellow basic sulfate, $2CuO.SO_3$, and finally cupric oxide[22]. The pentahydrate effloresces in dry air. It is precipitated from its solutions by the addition of glacial acetic acid. Copper sulfate forms well-defined double sulfates with many other sulfates (Zn, Mg, Cd, Fe, Co, Mn, etc.).

Anhydrous cupric sulfate is prepared by warming copper with concentrated sulfuric acid, by dissolving the pentahydrate in hot sulfuric acid and cooling, and also by cooling a saturated solution of the pentahydrate with solid carbon dioxide. It may also be prepared by heating of the pentahydrate at 250°C (480°F) *in vacuo.*

About 20 to 30 per cent of commercial cupric sulfate pentahydrate is a by-product of primary copper refining, and is made by crystallization of refinery liquids[23]. The cupric sulfate solution from the electrolytic cell is pumped to lead-lined tanks for evaporation and crystallization. Large amounts of copper sulfate are also manufactured by the so-called "oxidizer process" in which copper scrap is treated with hot dilute sulfuric acid in the presence of air. The spent solution is concentrated and cooled to produce the crystalline pentahydrate. Another method of producing cupric sulfate is by the leaching of a copper oxide ore with 100 per cent sulfuric acid. The ore is leached by percolation over a period of about eight days, or alternately heavy agitators are used. Undissolved material is removed by settling or filtration. The cooled solution is evaporated and crystallized[23].

Cupric sulfate pentahydrate is commercially available in various crystal sizes and grades of purity depending on the application. Impurities present in the technical salt depend upon the purity and source of the acid and the copper or its compound used as a raw material. When by-product sulfuric acid from copper refineries is employed, the impurities are usually reduced even in technical grades by recrystallization of the salt.

Basic cupric sulfate. Basic cupric sulfates differing in $CuO:SO_3$ ratio and degree of hydration have been reported. Knowledge of the basic cupric sulfates has been advanced by studies of *Bordeaux mixture,* $3Cu(OH)_2.CuSO_4$. The literature bearing on the composition of this and related fungicidal materials is discussed by Frear[30]. Bordeaux mixture is prepared by the addition of calcium hydroxide to a solution of cupric sulfate. *Burgundy mixture* (*Soda Bordeaux*) is made by the reaction of cupric sulfate with sodium carbonate.

Cuprammonium salts. A number of cuprammonium salts have been reported. The fungicide *Eau Celeste* is prepared by the addition of ammonium hydroxide to a solution of copper sulfate. During the reaction, the cuprammonium sulfate, $Cu(NH_3)_4SO_4.H_2O$, first formed is decomposed to a basic sulfate, possibly $2Cu(OH)_2.CuSO_4$, and ammonium sulfate. The nature and chemistry of *Eau Celeste* is reviewed by Frear[30]. Cuprammonium hydroxides, carbonates, and other salts have been prepared and studied as fungicides[29, 30].

Cupric sulfide, CuS, occurs as *covellite* or *indigo-copper*. When dry, cupric sulfide is stable in air, but is oxidized slowly to the sulfate in the presence of moisture. It is insoluble in alkali, but soluble in potassium cyanide solution. It can be prepared by treating a cupric salt with hydrogen sulfide or sodium sulfide. The suspension resulting is coagulated by hydrochloric acid to a pasty precipitate that is commercially available. Several cupric polysulfides (Cu_2S_3, Cu_2S_5, and Cu_2S_6) have been described, and cupric oxysulfides (*e.g.*, $CuS.CuO$, $2CuS.CuO$) have been obtained as by-products in the reduction of sulfuric acid to sulfur dioxide by copper.

Cupric sulfite. A hydrated basic cupric sulfite is known as a red-yellow amorphous powder which decomposes in boiling water to copper sulfate and other products.

Cupro-cupric sulfate dihydrate, $Cu_2SO_3.CuSO_3.2H_2O$, is known as red crystals. It is stable in air, but oxidizes to cupric sulfate and a basic salt when moist. A yellow pentahydrate is also known that passes to the dihydrate on boiling with water.

Cupric thiocyanate, $Cu(SCN)_2$, is formed as a brown-black precipitate when a solution of thiocyanate is added to a moderately strong solution of a cupric salt. It decomposes on storage, rapidly in the presence of water, into cuprous thiocyanate and other products. Many stable complexes are known. The literature on cupric thiocyanate is summarized by Williams[81] and by Beilstein[8].

Copper in the +3 Oxidation State

The literature concerning copper in the +3 oxidation state (tervalency) has been reviewed by Vrtis[74], by Scholder[62], and by Kleinberg[42]. Evidence for the existence of complexes of tervalent copper with tellurate and periodate groups has been reported[16, 48, 74, 121]. Evidence has also been reported[14, 45, 62, 75] for the existence of copper sesquioxide, Cu_2O_3, and the cuprate (III) ion, $[CuO_2]^{-1}$.

Complex Inorganic Compounds of Copper

Copper in all oxidation states shows a strong tendency to form complex compounds by coordination. In the cuprous state the coordination numbers of 2 and 4 are observed. In the cupric state the most common coordination number is 4, but 2 is not infrequent, and 6 (the limiting covalency) is reported for a few compounds.

Space in the present work does not permit a detailed discussion of the complex inorganic compounds of copper; however, the literature has been reviewed in recent years by Hückel[34], by Sidgwick[63], by Wells[79], and by Moeller[103].

Copper carbonyl. The existence of a copper carbonyl is suggested[103, 107] by the volatility of copper when heated in carbon monoxide[89] and by the precipitation of yellow copper-containing material from methanol prepared from carbon monoxide and hydrogen in the presence of a copper catalyst[107].

The Uses of Inorganic Cuprous Compounds

Although the uses of inorganic cuprous compounds are not as numerous as those of the corresponding cupric compounds, space does not permit a full listing. Other actual and potential uses of cuprous compounds are given by Gregory[31] and by Snell[67]. The fungicidal uses of cuprous compounds are described by Frear[30], and in Chapter 40.

Cuprous acetate (or its equivalent formed by the interaction of cuprous oxide and acetic anhydride) dissolved in pyridine or quinoline replaces halogen by hydrogen in certain aromatic compounds[120].

Cuprous cyanide has many applications. Its principal use is in electroplating baths containing alkali metal cyanides. It has catalytic activity in a variety of organic reactions, including isomerizations of hydrocarbons. In the Sandmeyer reaction it functions by replacing the $-N_2Cl$ group by $-CN$. Cuprous cyanide can also be used to replace halide groups in organic compounds with cyanide. Thus allyl cyanide is obtained in good yield from allyl chloride. Cuprous cyanide has been investigated as an insecticide, and semicommercially as a substitute for lead or magnesium arsenic compounds. Its complex with nicotine and hydrocyanic acid has been reported as an insecticide and a fluorescent material[66]. It has weak fungicidal properties. It may be sprayed on ship bottoms by suspension of a paste form in a suitable carrier[46], and incorporated in antifouling paints. It removes occluded oxides from molten copper and other metals[83]. For local application in trachoma and conjunctivitis, it has been employed in ointment or stick form.

Cuprous halides have found use as catalysts in a variety of organic reactions[9]. Cuprous halide complexes of nicotine have been claimed as insecticides or fluorescent materials[66].

Cuprous bromide displays catalytic activity like the other halides. It has been described as a component of carbon brushes for dynamos[19].

Cuprous chloride has many uses as a catalyst[9] and as a reagent in organic reactions (*e.g.*, the Sandmeyer reaction for conversion of aromatic amines to the chloro compound by diazotization, the Gatterman-Koch reaction, and the condensation of soaps, fats, and oils). Cuprous chloride finds extensive use as a catalyst, desulfurizing agent, and decolorizing agent in the petroleum industry. It catalyzes the formation of chlorine from hydrogen chloride and oxygen and has received attention as a catalyst in the production of acrylonitrile, a compound finding increasing application as a basic material for polymers and soil conditioners. Cuprous chloride can be used in the purification of acetylene, as an absorbent for the separation and recovery of dienes from hydrocarbon gases, as an absorbent for oxygen and carbon monoxide in gas analysis, as a precipitant for many alkaloids, for the denitration of nitrocellulose, and in the manufacture of colors for textile dyeing, for pyrotechnics, and for paint. It is also an ingredient of insecticidal compositions.

Cuprous iodide displays catalytic activity like the other halides (*q.v.*). It was formerly suggested as an emetic.

Cuprous oxide, besides being an important copper ore (*cuprite*), finds wide use as a fungicide, especially as a seed protectant. For this use, the finer yellow grade is preferred. It is also used as a spray or dust on agricultural crops[30], and it has been studied for the control of tomato defoliation. It finds extensive use in antifouling paints for steel and wood exposed to sea water. It is used in certain types of photoelectric cells and in the manufacture of ruby-red glass and of red glazes on ceramics. Like other cuprous compounds it has catalytic activity. Rectifiers of cuprous oxide (formed *in situ*) are common. Cuprous oxide is used as a mild reducing agent and is incorporated in certain brazing pastes. It absorbs about 30 per cent by weight of nitrogen dioxide, which may be removed by warm carbon tetrachloride or other inert solvent[57].

Cuprous phosphide is a component of phosphorus-copper alloys that are used for the deoxidation of metallic copper and in the manufacture of phosphor bronze[51], and as a getter in incandescent lamps.

Cuprous silicide deoxidizes and hardens copper and certain alloys.

Cuprous sulfide, in addition to being an important mineral source of copper, finds use in the preparation of cupric sulfate (*q.v.*), and has been described as a component of electrodes for thermoelements[26, 50]. Cuprous sulfide has catalytic activity and has been described as a catalyst in the cracking of dicylopentadiene.

Cuprous sulfite has been reported as a permanent anticryptogamic agent for vines[22].

Cuprous thiocyanate is an active ingredient of marine antifouling paints, and has been employed in the explosives industry in primer compositions. Its complex with nicotine has been claimed as an insecticide or fluorescent material[66].

The Uses of Inorganic Cupric Compounds

Of the two important oxidation states of copper, the compounds of the cupric state are of greater industrial importance. However, numerous chemical applications involve a change of valence. Space does not permit a full listing of the known uses of cupric compounds. Other uses are described in other chapters of the present work and a large number of potential and actual uses are given by Gregory[31] and Snell[67]. The fungicidal use of cupric compounds is described by Frear[29] and in Chapter 40.

Cupric acetate finds use in the manufacture of Paris green and other arsenical pigments, and as an analytical reagent. Of greater commercial importance are the basic cupric acetates. These are important ingredients of many catalytic preparations, especially those employed in oxidation reactions (*e.g.*, acetaldehyde and acetic acid from ethyl alcohol). Normal and basic cupric acetates are used in insecticidal and fungicidal formulations, as ceramic colors, as oxidizing agents in making indigo, as mordants for vat dyes, as ingredients of marking inks for metals, glass, and similar materials, and as components of plating baths.

Cupric acetoarsenite or *Paris green* was formerly an important green pigment, but the use of arsenical pigments has been largely prohibited by law because of their toxicity. Paris green was one of the first arsenicals used in commercial quantities as an insecticide, fungicide, and wood preservative. At present it finds little application as an insecticide on crop plants due to the development of safer insecticides; however, considerable amounts are still used as a larvicide to control mosquitoes and small amounts are still used in antifouling and special insect-proof paints.

Basic cupric arsenates have been employed in the control of fungi and insects, and have been studied in antifouling compositions.

Cupric arsenite or *Scheele's green* was formerly used as a green pigment in calico printing and for wallpaper and as an intestinal antiseptic in the treatment of anemia. It is employed to some extent in wood-preserving compositions and in mosquito control.

Ammoniacal cupric arsenite shows some promise as an agent for marine borer control.

Cupric borate finds use as a ceramic color that endures strong heat. It has been described as a component of dehydrogenation catalysts, as a pigment for oil paint, as an insulating and sealing medium for lead wires in lamps and mercury rectifiers, and as a fireproofing agent for wood. It is reported to be as hard as corundum. Its fungicidal, insecticidal, and parasiticidal activity has also been recognized.

Cupric halides have found use as catalysts in a variety of organic reactions[9].

Cupric bromide is used as a catalyst in many organic reactions, including polymerizations, esterifications, halogenations, hydrogenations, and isomerizations. It is employed as a photographic intensifier and oxidizer and as a brominating agent, and as a reagent. It has been studied as an agent for control of termites and as a visual relative humidity indicator when impregnated in silica gel.

Cupric chloride has many applications. Its uses as a catalyst are summarized by Berkman[9], and include oxidation of hydrochloric acid to chlorine by oxygen (Deacon process), production of ketenes, and various esterifications and halogenations. In the petroleum industry it is used as a deodorizing and desulfurizing agent, as a purifying agent, and as an ingredient of isomerization and cracking catalysts. It is employed as a mordant in dyeing and printing textiles, as an oxidizing agent for aniline dyestuffs, and as an ingredient of indelible, sympathetic, and laundry marking inks. It has been used in the metallurgical industry in the wet process for recovering mercury from ores, in the refining of copper, silver, and gold, as an ingredient of tinting baths for iron and tin, and in electrotyping baths for plating copper on aluminum. It is used in photography as a fixer, desensitizer, and reagent, and in pyrotechnic compositions as a color-producing agent. It has been used occasionally in medicine as a substitute for cupric sulfate for its astringent and antiseptic properties and in veterinary medicine as a disinfectant for murrain in cattle. It has been studied as an ingredient of insecticidal compositions and wood preservatives.

Basic cupric chlorides (copper oxychloride) are important ingredients of some commercial fungicidal preparations that are applied to crop plants by spraying or dusting. Basic cupric chlorides have catalytic activity and have been investigated as catalysts in the Deacon process and in many organic reactions.

Cupric chlorate has been used as a mordant in dyeing and printing of textiles.

Cupric fluoride has been used as an opacifier in enamels, glass, and ceramics, as an ingredient of welding and brazing fluxes, and as an additive (1 per cent) to cast iron to improve strength and wearing qualities. Basic cupric fluorides have been studied in fungicidal compositions.

Basic cupric carbonates find many applications. The natural occurring basic carbonates malachite and azurite when ground have been widely used in seed treatment and as a smut fungicide. They have also been employed as green to blue pigments. The much prized patina on weathered copper or bronze approximates a basic cupric carbonate. Commercial basic cupric carbonate finds application as fungicides (Soda Bordeaux or Burgundy mixture), and as an ingredient of insecticidal, snail-control, and rabbit-repellent compositions, as a pigment in paint, varnish, and ceramics, as an agent promoting adhesion of bituminous aggregates, as a pickling agent imparting a black color to brass, as an ingredient of pyrotechnic compositions, and as a raw material in the manufacture of other copper compounds. Basic cupric carbonates have been used in medicine as astringents and as antidotes for phosphorus poisoning. **Cuprammonium carbonate** has been used in the manufacture of mixed catalysts.

Cupric chromates are used as mordants in dyeing. Acidic cupric chromates show promise as agents in marine borer control. Impregnation of textiles with an ammoniacal solution of copper chromate has been claimed to protect insects and microorganisms. Cupric chromates have been studied as electrical resistors and mixed chromates with cobalt, zinc, and other metals have activity as seed protectants and as crop fungicides.

Cupric chromite catalysts have received attention in recent years as a selective hydrogenation catalyst for organic compounds[2, 3]. **Cupric ferrocyanide** is used as a pigment (Hatchett's or Mahogany Brown) and in photographic toning baths. Its use to restrict the deposition of reflected coatings to desired areas in the manufacture of glass and plastic mirrors has been patented[114]. The use of a cupric ferrocyanide gel (formed *in situ* by the interaction of cupric sulfate and ferrocyanide solutions) to lower the electrical resistance of soils and of electrode-to-soil contacts (lightning rods, transformer neutrals, etc.) has been described[85, 110].

Cupric nitrate hydrate and **basic nitrates** are used in light-sensitive reproductive papers, as a ceramic color, as a mordant and oxidant in textile dyeing and printing, as a reagent for burnishing iron and for coloring copper black, zinc brown, and for imparting a verde antique finish on copper, as an ingredient of nickel-plating baths and of pyrotechnic compositions, and as a component of paints and varnishes. Cupric nitrates and basic nitrates have been used as ingredients of sympathetic inks and of compositions for the control of weeds, fungi, and termites. These compounds have catalytic activity, and cupric nitrate has been found to be an effective nitrating agent for aromatic organosilicon compounds. It is a reagent in the preparation of special purity cupric oxide and of mixed catalytic preparations.

Cupric oxide (black oxide of copper) has extensive applications. It is used for the preparation of "cuprammonium hydroxide" solutions used in dissolving cellulose for the production of rayon. It is employed in glazes, glass, ceramics, and enamels as a coloring agent. It is an ingredient of pyrotechnic starting compositions, of welding fluxes for bronze, of metal cleaners, and of antifouling paints. It is used as an oxidation and reduction catalyst and as a catalyst for the desulfurization and purification of petroleum products. It serves as a cathode depolarizer in the electrolysis of alkali metal halides, as a positive electrode and depolarizer in primary cells, and as a rectifier. It finds use in the determination of carbon in organic compounds and in gas analysis (often in a high-purity wire form). It serves as a flux in the reverberatory refining of copper to reduce arsenic and sulfur. It is used for coloring artificial gems and as an exciter in phosphor mixtures. It serves as a raw material for the production of many other copper compounds. It has some fungicidal and insecticidal activity, but such activity has received little commercial attention. In medicine it was formerly used as a discutient in lymphadenitis, and it is reported to be a teniacide of low toxicity.

Cupric hydroxide is used as a mordant and pigment. It is used in the manufacture of many copper salts and for staining paper. It has been employed in rayon manufacture, for the treatment of paper, and in the preparation of Schweitzer's reagent. It is used in the manufacture of battery electrodes and as an ingredient of fungicidal and insecticidal compositions. It has some catalytic activity and has been used in the manufacture of mixed catalytic compositions.

Cupric phosphate has been studied as an agricultural fungicide. **Cupric selenide** has been used as a catalyst in Kjeldahl digestion. **Cupric silicofluoride** (cupric fluosilicate) has been used for treating plant diseases and for dyeing and hardening white marble.

Cupric sulfate pentahydrate is the chief chemical of copper. Of the 106,444 short tons shipped in the United States in 1951, 42 per cent went to agricultural uses, about 15 per cent went to the mining and metal industry, and the remainder to miscellaneous uses. The usual technical grade of the pentahydrate offered in the United States is better than 99 per cent in purity (copper content, 25.2 per cent). The U.S.P. grade contains not less than 98.5 per cent of the pentahydrate, and the reagent grade assays about 99.8 per cent pentahydrate. Test methods for cupric sulfate and other copper compounds for agricultural use have been established by A.O.A.C., and standards and tests for reagent grades of copper compounds by the American Chemical Society.

At one time, cupric sulfate pentahydrate had extensive fungicidal use. However, since 1885-1886 with the introduction of Bordeaux mixture its direct use has fallen off. The preparation and fungicidal activity of cupric sulfate and related compounds have been discussed by Frear[29, 30]. Other agricultural applications of cupric sulfate include addition to soil (directly or in fertilizers) to treat copper deficiencies in crops or animals or to improve specific crop yields. It is also used to kill potato vines at harvest, and as a herbicide. Cupric sulfate monohydrate in recent years has found commercial application as an agricultural fungicide, either alone or admixed with lime.

The minor uses of cupric sulfate pentahydrate are too numerous for listing in the present work. Some of those more frequently cited are given below. The extensive use of cupric sulfate as a raw material for the synthesis of other copper compounds has been noted in the earlier pages of this chapter.

Cupric sulfate is used as a mordant in textiles and in the preparation of azo dyes. It finds some use as a pigment in paints, varnishes, and other materials. It is an ingredient of electroplating solutions, of battery electrolytes, of mordant baths for intensifying photographic negatives, of pyrotechnic compositions, of water-resistant adhesives for wood, of laundry-marking and metal-marking inks, of wood-preservative compositions, of metal coloring and tinting baths, of antirusting compositions for radiator and heating systems, and of various mixed catalysts. It is used for treating leather to permit the use of basic dyes, and as a reagent or toner in photography and photoengraving. Cupric sulfate pentahydrate is an official drug in the United States and British Pharmacopoeias. Its chief therapeutic use is as an irritant, astringent, and antiseptic. It has limited use as an emetic. However, in phosphorus poisoning it acts as a chemical antidote as well as an emetic. A 1 per cent solution is valuable in the topical treatment of phosphorus burns. It has also been employed as a cattle parasiticide and in a number of veterinary medical applications.

Anhydrous cupric sulfate is used for detecting the presence of trace water (blue color) in alcohols and other organic compounds and for drying these substances. **Basic cupric sulfates** are employed as agricultural fungicides. Their use and preparation have been reviewed by Frear[30].

Cupric salts of organic acids are of industrial importance (see also cupric acetate). Cupric citrate and gluconate find use in medicine, the first as an antiseptic astringent and the latter as a readily assimilable form of copper. Copper soaps (oleate, stearate, resinate, and naphthenate) are used in antifouling paints and in textile and wood preservatives. Copper undecylenate is used in the treatment of skin diseases. Cupric sebacate is stated to be of special interest in connection with coatings and to have marked fungicidal properties[126].

Cupric ammonium silicate has been manufactured for use as an agricultural fungicide. It appears to be a complex of cupric sulfate, sodium silicate, and ammonia[30].

Cupric sulfide in paste form has found use for the development of aniline black in textile printing. It has also limited use in antifouling paints, and in the preparation of mixed catalysts. A complex **potassium**

cupric ferricyanide pigment having a beautiful maroon color has been described[95].

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Chapter 40

Copper as an Agricultural Fungicide

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Copper is used to a greater extent in the preparation of agricultural fungicides than any other metal, and as such it is chiefly utilized as a component of numerous inorganic compounds. Its use in fungicides of an organic nature is comparatively limited for agricultural purposes. In spite of the fact that copper is so widely used in fungicidal formulations, it is not the most fungitoxic of the metals. It is exceeded in this respect by silver, mercury, and cadmium[11], among others. The popularity of copper compounds as fungicides is largely due to a fortunate combination of a fairly high degree of fungitoxicity, a comparatively low degree of toxicity to most higher plants and animals, and a lower price than most other metals of comparable effectiveness in disease control. Sulfur is less costly pound for pound than copper, but it possesses less universality as a fungicide. In the field of organic fungicides used in agriculture, copper is less utilized as the metal portion of that group of compounds than is mercury or zinc.

The fact that copper is capable of checking plant diseases was first mentioned by Schulthuss[20] in 1761 when he reported that soaking the seed of cereal crops in a solution of copper sulfate in water would retard the development of bunt and other smuts. However, the use of this treatment for these cereal diseases developed slowly until nearly 50 years later when Prevost[16] in 1807 found that the germination of the spores of the causal organism of bunt could be inhibited by very low concentrations of copper (as little as 1 ppm). This small but important bit of information was followed by a rather rapid increase in the use of copper sulfate as a cereal seed treatment. It was approximately a century later that copper sulfate began to be replaced for this purpose by copper carbonate, and shortly thereafter[4] the practice of soaking as a means of treating the grain seed began to be replaced by a dry (dust) treatment. The first of these dust treatments contained a finely divided copper carbonate as the active ingredient. This was soon followed by various organic compounds, most of which contain no copper, but several of which do contain mercury.

Early Copper Fungicides

Copper Sulfate. Copper sulfate, $CuSO_4.5H_2O$, which is used in the preparation of numerous fungicidal compounds, is an excellent fungicide in its own right. However, it is little used on plant foliage because of its high degree of phytotoxicity. It is used in a few instances on dormant plants. In normal times well over half of the annual production of copper sulfate is utilized in one way or another by agriculture. Of that used in fungicides, possibly 50 per cent goes into the preparation of Bordeaux mixture, much of which is now used for the spraying of such tropical crops as banana, coffee, tea, rubber, and various species of citrus. The remainder is consumed in a variety of ways. Some of these in addition to fungicides are as a wood preservative, as a nutritional soil additive, for treating seeds, to rid ponds and lakes of unwanted vegetation, as a weed and vine killer, and as one of the ingredients of certain insecticides.

Had copper compounds been limited in their use as agricultural fungicides to the treatment of grain and vegetable seeds, the total today would represent a comparatively small volume. Since much of the copper used in fungicidal preparations is first in the form of copper sulfate, estimates of the quantity so utilized is usually stated in terms of $CuSO_4$ (the metallic equivalent being one-fourth of that amount). Published estimates by various authors[5, 12] made for the period between 1940 and 1945, when the annual use was possibly as large as at any other time, range from 75 to 100 million pounds for the $CuSO_4$ equivalent in the United States alone to 500 or more million for the world total. From 50 to 75 million pounds is used each year on bananas, principally in Central America, and large quantities are also applied to such warm-climate crops as rubber, tea, coffee, cacao, and citrus species. Copper in various forms is still the most used fungicide in Europe and various other parts of the world, and thus the total annual world use in agricultural fungicides probably still exceeds 350 million pounds in terms of $CuSO_4$.

Bordeaux Mixture. An outbreak of downy mildew in the vineyards of France about 1878-1880 furnished the necessary incentive to a search for control measures to save the grape crop and with it the wine industry. A few years later it was observed that a paste, prepared by mixing a rather concentrated solution of copper sulfate with a suspension of lime in water, applied heavily to grapevines to deter pilfering of the fruit by passersby, was also checking the development of mildew. This combination of copper sulfate and lime and its effect on the initiation and development of grape mildew was described by Millardet in 1885[13] and given the name of Bordeaux mixture.

This mixture, which is generally credited with being the most universally effective fungicide ever developed, has undergone considerable change in formulation during the 70 years that have elapsed since the more or less accidental discovery of its ability to control downy mildew of grapes. Some of the early formulas called for the use of what would today be considered fantastically large amounts of copper sulfate and quicklime in each 100 gallons of water. Experience, and the replacement of slaked or burnt lime by the hydrated form, has since resulted in the adoption of such standard formulas as a 10-10-100 (10 pounds of copper sulfate and 10 pounds of hydrated lime in 100 gallons of water), 8-12-100, or 8-8-100 for use on Bordeaux-tolerant vegetables and various other crops. Other formulations as weak as 6-6-100 or even 4-4-100 are recommended for use on Bordeaux-sensitive plants such as cucurbits, beans, etc. On fruits the formula may be as dilute as 1-2-100. The comparatively recent introduction[10] of powdered copper sulfate has made it possible to prepare Bordeaux mixture quickly by placing the powdered copper sulfate on the screen of the sprayer tank and washing it into the tank already containing the necessary amount of hydrated lime suspended by constant agitation in a quantity of water that represents at least half the final volume of the spray mixture.

During the time these changes in the physical constitution of Bordeaux mixture were going on, there was much investigational work in progress on the chemical composition of the end products of the reaction (or reactions) which takes place when these two comparatively simple chemical compounds are brought together in the presence of water.

A complete review of the voluminous literature now available on the chemistry of Bordeaux mixture[1, 10, 15] would be out of place here. It is rather generally accepted that the reaction that takes place as solubilized copper sulfate is added to a suspension of hydrated lime in water is somewhat as follows:

$$CuSO_4 + Ca(OH)_2 \rightleftharpoons Cu(OH)_2 + CaSO_4$$

The tendency of $Cu(OH)_2$ to decompose is checked or stabilized by the presence of $CaSO_4$. The final mixture may be acid, neutral, or alkaline, depending on the ratio of the amount of copper sulfate to that of hydrated lime. However, nearly all of the Bordeaux formulas now in common use are alkaline, and seldom if ever acid, or even neutral. However, what may be considered as excessive lime is no longer used in the preparation of these formulas for most crops, and particularly vegetables, because of the increased likelihood of spray injury. A slight excess of lime is sometimes used in spraying fruit trees to reduce the chance of copper injury.

Bordeaux mixture should be freshly prepared each time it is used, since it deteriorates rather rapidly on standing. It soon begins to lose its gelatinous nature and the physical character of the precipitate changes to a more crystalline form; adhesion and fungitoxicity both decrease. The addition of sugars, albumins, organic acids, etc., help to delay the physical and chemical changes that take place with time, but these adjuvants seldom are used since the average grower who uses Bordeaux prefers to prepare it each time he wishes to make a spray application. It is interesting to note that Bordeaux mixture is now used to control diseases on at least 50 different crops in the United States[12], and many more the world over.

Dry Bordeaux. The small grower often does not wish to go to the trouble to prepare a solution of copper sulfate and a suspension of "fresh" hydrated lime each time he is to spray a few plants, and this has created a somewhat limited (and now decreasing) demand for a "dry" Bordeaux mixture that may be weighed out in small quantities and readily mixed with something like 1 to 10 gallons of water. This dry preparation, which is formulated to contain about 13 per cent of copper, is not nearly as effective in disease control as the usual form of freshly prepared Bordeaux mixture, but the home gardener, who is the principal user, usually is willing to sacrifice a certain degree of effectiveness for the sake of convenience.

Burgundy Mixture. Burgundy mixture, like Bordeaux mixture, received its name from the place in France where it was first used, in 1887[3]. It is prepared by adding sodium carbonate to a solution of copper sulfate. The blue precipitate that is formed is basic copper carbonate. Burgundy mixture adheres well to plant foliage and is an excellent fungicide, but it is almost too phytotoxic for use on many plant species. The most commonly used formula is 10-10-100, but it is sometimes prepared in more concentrated formulations. It is now little used as a fungicide, largely because it is more costly and somewhat less durable after application than Bordeaux mixture.

Miscellaneous Mixtures. Several copper-containing spray mixtures were developed and introduced within a few years after Bordeaux mixture. These included among others the neutral and basic copper acetates and basic copper carbonate (both discussed under the fixed coppers), and such formulations as Cheshunt compound or Johnson's mixture, Eau Celeste, and copper ammonium carbonate. Cheshunt compound is made by first preparing a physical mixture of powdered copper sulfate (2 parts) and ammonium carbonate (11 parts) and then adding this to water. Eau Celeste is prepared by adding ammonium hydroxide to copper sulfate. Copper ammonium carbonate is formulated by adding ammonia to copper carbonate. None of these preparations has ever been very widely used as a fungicide in the United States, largely because Bordeaux mixture is cheaper, safer, and for most purposes a better fungicide.

Copper-lime Dust. Copper-lime dust forms what is essentially Bordeaux mixture in the presence of moisture in the form of dew or rain after it is applied to the plant. It is commonly prepared by mixing 20 parts of monohydrated copper sulfate ($CuSO_4.H_2O$) with 80 parts of freshly hydrated lime. It then has to be stored in an airtight container until it is used to prevent the absorption of water by the monohydrated copper sulfate and the carbonation of the lime, which would occur in the presence of air. The fact that this dry mixture could be substituted for Bordeaux on many plants was reported just previous to 1920[18]. It was widely used, especially on certain vegetable crops, during the next few years, after which it was gradually replaced by fixed-copper dusts. These are prepared with inert diluents such as clays, talcs, infusorial earth, finely ground limestone, etc., and can be stored without appreciable deterioration in ordinary containers. Dusting as a general practice is now rapidly losing favor, partially due to the advent of concentrate spraying, either with a supplementary air blast or by the usual hydraulic means.

The Fixed Coppers

The development of the so-called "fixed" or "insoluble" copper compounds, which are generally considered to be less phytotoxic than Bordeaux mixture, began about 1930, and was undoubtedly accelerated by the constant accumulation of evidence showing that various crops were injured more than previously realized by the application of Bordeaux mixture[22]. The list of the fixed coppers grew rapidly from 1930 until about 1940[24], after which the introduction of new compounds was slowed down by the scarcity of copper during the second World War, and the introduction about that time of a series of specific but highly fungitoxic derivatives of dithiocarbamic acid.

The exact chronological order in which these copper compounds, most of which may be classified as "fixed" coppers, was introduced is difficult to determine in some instances. Basic copper acetate and basic copper carbonate preceded 1930 by several years, but neither ever came into very general use as a fungicide. Shortly after 1930 such compounds as copper phosphate, cuprous oxide, copper silicate, copper ammonium silicate, copper zeolite, copper oxychloride, basic copper sulfate, brown cuprous oxide hydrated, copper hydroxide or hydrate, basic copper arsenate, copper oxychloride-sulfate, and copper-zinc chromate were brought out in approximately that sequence.

Cuprous oxide (red and yellow) was one of the first of the fixed-copper group to be used in appreciable volume. It was first used as a seed treatment[9] and later as a foliage spray. The copper oxychlorides were among the first to be used in any quantity in Europe and these became popular in America shortly afterward. One compound which combines low cost, mild phytotoxicity, and a fair degree of fungitoxicity is tribasic copper sulfate, and this has come to be the most widely used of this general group of copper compounds. A combination of the oxychloride and the basic sulfate[25], which combines the fungicidal activity of the former and the safety of the latter, and designated as copper oxychloride-sulfate, has been used in considerable quantity during the last 15 years.

Basic Copper Acetate, $Cu(C_2H_3O_2)_2.CuO.6H_2O$. This material was introduced in France in 1889 as a grape fungicide[2]. It was followed in 1892 by the neutral form, $Cu(C_2H_3O_2)_2.H_2O$. Neither has ever been much used as a fungicide in the United States. They are comparatively safe on most plants and leave little visible spray deposit. Both forms are excellent fungicides, but they do not adhere as well as Bordeaux, and are more costly. They are commonly formulated as spray mixtures to contain about 2 pounds of copper acetate in 100 gallons of water.

Basic Copper Carbonate, $Cu(OH)_2.2CuCO_3$. This compound, which is commonly prepared by adding sodium carbonate to copper sulfate, was first used on wheat seed for the control of bunt about 1902. However, it did not become widely known or used as a seed-treating material until it was recommended in the form of a dust treatment by Darnell-Smith in 1917[4]. Following that date its use increased rapidly for several years, after which it was largely replaced by various organic fungicides.

Copper Phosphate, $Cu_3(PO_4)_2.3H_2O$. This compound[6] is comparatively insoluble in water and adheres rather poorly to plant foliage. It gives somewhat better disease control when prepared as a "tank-mix" product by adding Na_3PO_4 to a solution of copper sulfate in water during constant agitation, under which conditions it forms a gelatinous precipitate that is more adhesive than the dry powder. It is much inferior to Bordeaux as a fungicide and has never come into very general use.

Copper Ammonium Silicate (definite formula not known). This material[21] is produced by allowing copper sulfate to react with 5 parts of sodium silicate and 1 part of ammonium hydroxide. It is comparatively low in phytotoxicity, of low solubility, highly buffered, and of at least medium fungitoxicity. It has never been widely used as a fungicide.

Copper Oxychlorides, $3Cu(OH)_2.CuCl_2$ and $2Cu(OH)_2.CuCl_2$. Prepared as fungicides[28] these materials were among the first of the fixed coppers to be widely used in the United States. They had been used to a considerable extent for several years in Europe before their introduction to this country about 1930. There are several commercial formulations now available and they have been rather generally recommended for the control of a variety of vegetable diseases. They are more or less intermediate in phytotoxicity among the fixed coppers and may be classed as good fungicides. Some of the difficulties encountered in their manufacture, and their cost, have perhaps prevented them from coming into more general use.

Tetra Copper Calcium Oxychloride (definite formula not known). This oxychloride is an excellent fungicide, but it is somewhat more phytotoxic than the general run of fixed coppers. Also, on a copper equivalent basis (45 per cent) it is slightly more expensive than various other oxychlorides and tribasic sulfates. However, it is usually recommended at the same concentration as other compounds of higher copper content, and thus part of the extra cost is thereby discounted. It is especially effective in the control of certain diseases of potato, tomato, celery, etc.

Copper Oxychloride-sulfate, $7Cu(OH)_2.CuCl_2.CuSO_4.xH_2O$. This fungicide[25] is a mixture made up of approximately 2 parts of basic copper sulfate and 1 part of basic copper chloride. It was tailor-made to provide a material that would combine the plant safety of the former with the fungitoxicity of the latter. It is an excellent fungicide that adheres comparatively well to plant foliage, and it has given good control of a considerable variety of plant diseases, some of those of vegetables in particular.

Copper Hydroxysulfate (definite formula not known). This compound is highly fungicidal and somewhat phytotoxic. Difficulties encountered in manufacture, and a comparatively high price, have been instrumental in limiting its use as a fungicide.

Basic Copper Sulfate and/or Tribasic Copper Sulfate, $CuSO_4.2Cu(OH)_2.xH_2O$. Basic copper sulfate[8] is one of the least phytotoxic of the fixed coppers that are commonly used for the control of plant diseases. This characteristic, combined with the fact that it can be manufactured and sold as cheaply as any, with one or two possible exceptions, has made it one of the most widely used of the fixed coppers. One of its principal uses has been on crops that are especially sensitive to injury by Bordeaux mixture. It adheres well when of small particle size, and is compatible with many of the modern insecticides. It has been widely used in dust formulations, where it is also compatible with a wide range of diluents and conditioning agents.

Cuprous Oxide, Cu_2O. Cuprous oxide varies in color from red to yellow, depending upon the size of the individual particles. The red material has an average particle size of approximately 2.5 microns, and it changes from red to yellow as the particle size approaches 1 micron. Cuprous oxide is an effective fungicide with good adhesive qualities. The yellow form adheres nearly as well as Bordeaux mixture, which is considered to represent the maximum adhesion available among the common run of copper fungicides. The copper content varies from 75 to 85 per cent in different formulations. Cuprous oxide was suggested as a seed treatment material by Horsfall[9] about 1932 and a considerable amount of it was used for that purpose for a number of years. However, it has now been largely replaced for use on seeds by various organic compounds. It is somewhat phytotoxic to numerous plant species and care should be taken not to apply it in excess.

Cupric oxide (CuO) is more phytotoxic than the cuprous form and varies in color from brown to black. It is much less effective as a fungicide. A considerable variety of cuprous oxide preparations are now available for use as fungicides. Some of these are nearly pure cuprous oxide, others contain some cupric oxide, and in one form the cuprous oxide exists as a thin coating over a metallic copper core. A hydrated cupric oxide ($4CuO.H_2O$) has also been prepared for use as a fungicide.

Copper Zeolite (definite formula not known). This is a complex copper aluminosilicate[14] of rather indefinite composition and somewhat difficult to manufacture. It is prepared from sodium silicate, sodium aluminate, and copper sulfate. It is of low solubility, an effective fungicide, and comparatively safe on most plants. However, it has never been widely used for various reasons, chief among which are the difficulties involved in its manufacture and its comparatively high cost.

Basic Copper Arsenate, $Cu(CuOHAsO_4)$. This arsenical is safer on foliage than most, but phytotoxicity due to copper may be comparatively severe on copper-sensitive fruits and vegetables. Adhesion is good and the compound is a fairly good fungicide, but it has never come into very general use as either a fungicide or an insecticide.

Copper Phthalate. This material has been experimentally tested for disease control. It proved to be only mildly fungicidal in field trials and was somewhat phytotoxic.

Copper Nitrate, $Cu(NO_3)_2$. This compound is too phytotoxic for use as a fungicide, but it can be used as a weed-killer.

Cuprous Cyanide, $Cu(CN)_2$. This material can be used as an insecticide, but very little use has been made of it for this purpose, or as a fungicide.

Copper 8 Quinolinolate, $Cu(C_9H_6O.N)_2$. This compound, which is prepared by the precipitation of a copper salt with 8-hydroxyquinoline, was intended as a fungicide on vegetable crops, but it is far too expensive for general use. Attempts to so formulate it that it could be used in low concentrations, and thus be competitive pricewise, have failed in that fungicidal effectiveness was lost when dilution was sufficient to make a spray formulation that the grower could afford to use. It is now widely used as a surface fungicide for damp walls, and on fish nets and various fabrics.

Copper-zinc Chromate Complex, $15CuO.10ZnO.6CaO.25H_2O$ (30 per cent Cu, 20 Zn, and 10 Cr). This complex of copper and zinc combined in a chromate[7] is highly insoluble in water, comparatively safe on many plants, and of high fungitoxicity. It has the ability to control a variety of plant diseases, but is used as a fungicide principally on vegetables and a few zinc-tolerant fruits. It also has some value as a seed protectant. As a fungicide it has been considerably used on certain specific crops where it has had to compete with various other copper-containing and organic compounds, many of which are less costly than the copper-zinc chromate.

Copper Resinate. The organic copper salt which has the empirical formula $Cu(C_{20}H_{20}O_2)_2$ is comparatively low in copper. It has been prepared for foliar application as a fungicide[5] by solubilizing it in pine oil, and in various mineral oils. It leaves comparatively little visible residue on the leaves, but has been used very little in plant disease control. It has been utilized in the paper industry to check the growth of fungi in certain types of material used for packaging foods.

Copper Naphthenate. This compound, which is produced by the interaction of a copper salt and naphthenic acid, is too phytotoxic for general use on plants, although it is an excellent fungicide. It cannot be formulated as a spray material without being specially processed, usually with a mineral oil, and an emulsifying agent. Experimental work is now in progress on the possibility of so formulating it with a vegetable oil that it can be used as a foliar fungicide. It is now commonly used to treat wood, as in fence posts and railroad ties, as a well sterilant, and for the preservation of fish nets and various fabrics that are exposed to severe weathering.

Various Other Organic Copper Salts or Soaps. A considerable number of these, such as copper stearate, oleate, salicylate, laurate, etc., have been tested as plant fungicides. Most of them are difficult to formulate and not very effective as fungicides. None have ever been used to any considerable extent in the control of plant diseases.

Formulation

The manner in which the copper fungicides are formulated, or prepared for use, is often an important factor in determining their effectiveness in *disease control and their degree of phytotoxicity to the host plant.* For instance, the relative and actual quantities of copper sulfate and hydrated lime that are used in the preparation of Bordeaux mixture are frequently varied to fit it better for use on both tolerant and sensitive host plants. High-lime Bordeaux is usually more injurious to plants than a formula in which the quantity of lime used is equal to, or slightly less than, that of the copper sulfate. Sugar, molasses, and various other materials may be added to Bordeaux to delay the normal progress of crystallization and oxidation that commonly proceeds with aging and exposure to weathering. Also, an oil emulsion may be added to check the increased loss of water by transpiration which is frequently brought about when Bordeaux is applied to plant foliage. Copper acetate may be formulated as a basic or neutral mixture by altering the relative proportions of acetic acid and copper used in its preparation. The two forms then possess somewhat different properties with respect to plant injury and disease control.

The "fixed" or "insoluble" coppers as a group adhere to plant foliage much less tenaciously than Bordeaux mixture, as indicated by the fact that 80 per cent of a properly prepared Bordeaux may still be present on a tomato leaf after being subjected to an inch of artificial rain, whereas the most adhesive of the fixed coppers (a finely divided cuprous oxide) will not exceed 70 per cent of the original deposit under the same conditions, and some of them may show a retention of no more than 20 per cent. Most of these copper compounds adhere much better when applied as sprays than as dusts, nearly twice as well in most instances. Particle size is an important factor in determining adhesion, and in general the finer these compounds are prepared the better they adhere.

A wide variety of adhesives has been tested in a search for one that might make a material such as tribasic copper sulfate or copper oxychloride applied as a spray adhere to plant foliage as well as Bordeaux, but to date it is doubtful if any such adhesive is available. Among the best are bentonite, various plastic emulsions, polyethylene polysulfide, various oil-containing mixtures, and some of the new polyelectrolytes such as those used as soil conditioners. It frequently happens that some of the best adhesives increase plant injury by the fixed copper to the point where phytotoxicity may be even more apparent than that caused by Bordeaux under the same conditions.

As stated above, dust formulations of the fixed coppers adhere less well than sprays, but the adhesion of the copper fraction can be varied rather widely by the selection of the diluent used in preparing the dust[26]. For instance, most clays adhere better than the talcs, and a finely ground bentonite is one of the best dry powders available for this purpose. However, a dust formulation prepared by mixing a fixed copper and bentonite would be highly phytotoxic. Thus, compatibility and plant safety must be considered, and a compromise between these factors and adhesiveness usually has to be made.

Crops and Diseases

Copper-containing compounds are used on nearly all of the economic plants that are commonly sprayed or dusted for the control of those foliage diseases that can be prevented in that way. A host inventory would include at least 100 species of comparatively important crop and ornamental plants on which copper fungicides are, or have been, used. They have been especially useful in controlling certain foliage diseases of potato, tomato, celery, apple, grape, cherry, banana, citrus species, tea, coffee, cacao, and hops, as well as others too numerous to list here. They also have been widely used as a seed treatment to improve the stand of seedlings and to control various seed-borne diseases of crop plants.

Bordeaux mixture, which is considered the world's most useful and versatile fungicide, is used to control the diseases of more different host plants than any other fungicide formulation. It is no longer, however, the first choice for the control of many of the diseases against which it is effective because of its tendency to injure various sensitive plants, such as tomato, several of the cucurbits, apple, peach, grape, etc., as well as the seeds of crucifers, beans, and others. Part of the impetus for the development of the fixed coppers may be attributed to the need for less phytotoxic compounds of copper for use on Bordeaux-sensitive species. However, Bordeaux mixture will always be remembered for the part it has played in saving and making it possible in years past to grow larger quantities of such crops as grapes, bananas, potatoes, and many others.

Future Use

As has been indicated earlier, the copper-containing fungicides as a group are meeting very serious competition from a comparatively new series of materials of organic nature for use in the control of a wide variety of plant diseases, particularly those of fruits and vegetables. On fruit, where copper has never been as widely used as sulfur, any copper compounds formerly used are being gradually replaced by various organic fungicides. On vegetables such as potatoes, tomatoes, and celery, the use of copper has decreased steadily since about 1945[27], at which time the dithiocarbamates began to appear on the market. Iron, zinc, and manganese dithiocarbamates are now being widely used on these three and many other vegetables, whereas the copper-containing derivatives of dithiocarbamic acid, which are more phytotoxic and less fungitoxic, are seldom recommended. Ziram (zinc dimethyl dithiocarbamate) is now recommended on the cucurbits to replace the somewhat more phytotoxic copper compounds, and ziram and other dithiocarbamates are being used on tomato to give better control of anthracnose fruit rot than is afforded by copper. The ethylene bis-dithiocarbamates that contain zinc or manganese have replaced, to a considerable degree, Bordeaux mixture and the fixed coppers, even on copper-tolerant crops such as potato and celery.

On crops such as banana, rubber, coffee, tea, and even citrus that are grown largely in the tropics, under environmental conditions that demand a maximum of stability, durability, and adhesion, Bordeaux mixture, and to a lesser extent the fixed coppers, are still regarded as more reliable from the standpoint of disease control than are any of the organic fungicides so far tested. The most recent recommendations* indicate that Bordeaux mixture is still the outstanding fungicide for use on bananas, and this and other copper-containing materials are widely used to control various diseases on coffee, citrus, and tea. Although rubber may not be as commonly sprayed for disease control because of mechanical difficulties experienced in spraying tall trees, it is usually treated with Bordeaux mixture.

Another interesting development has been the recent shift back to Bordeaux, and to a less extent the fixed coppers, on potatoes to replace, just at the end of the season, whatever dithiocarbamate had been used earlier, in an effort to hasten maturity and give a maximum of protection against late-blight tuber rot.

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* These were corroborated by recent correspondence with the following: citrus species, R. F. Suit, Citrus Experiment Station, Lake Alfred, Florida; banana, N. C. Thornton, United Fruit Company, La Lima, Honduras; coffee, R. V. Norris, Coffee Research Station, Kenya Department of Agriculture, Nairobi; tea, R. W. Rayner, Tea Research Institute of Ceylon, St. Coombs, Talawakelle, Ceylon.

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Chapter 41

Cupreous Powder and Its Applications

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Cupreous powder as an industrial product is derived from the precipitate which forms when iron replaces copper in solution. Nearly everyone has dipped a steel nail into a solution of copper salt and watched it become coated with copper. The phenomenon has been observed since early in the fourth century[1] and was considered by the alchemists to be a transmutation of the baser metal to copper. "Cementation," so named because the copper is considered to "cement" out on the iron, was employed during the fifteenth century[2] at the Rio Tinto deposits in Spain and somewhat later in Peru. Its use in this country probably started in 1889 when a resourceful neighbor put scrap iron and old cans in ditches that carried the run-off from copper operations in Montana. Today more than 70 million pounds of copper precipitate or "cement" copper is produced annually in five Western states[3] and this amount increases as poorer ores are exploited. Usually this copper is dissolved from the low-grade ores or wastes as copper sulfate and is precipitated on iron, preferably shredded cans from which organic debris has been burned. It is removed from the precipitating tanks or launders in the form of dendritic clusters of metallic copper contaminated with other metal sulfates and the minerals dissolved from the ore plus those inherited from the scrap iron. A typical analysis of high-grade precipitate is given in Table 41-1[4].

The copper precipitate is dried and added to the charge which goes to a smelting furnace to produce matte[5]. Its fineness makes it difficult to smelt without excessive loss and imposes a limit upon the amount that can be added to a charge.

The failure over the years to recognize this copper precipitate as a useful product rather than as a crude can be explained by the fact that as the material dries it blackens and sometimes burns, since extremely fine copper, when exposed to air while damp, oxidizes through cuprous to cupric oxide at a rate that results in heating. Masses from which this heat cannot escape fast enough will reach ignition temperatures, and attempts to ship damp precipitate have sometimes resulted in loss of box cars.

Table 41-1. Typical Analysis of High-grade Copper Precipitate

	Per Cent
SiO_2	0.361
CaO	.038
Al_2O_3	1.797
P_2O_5	.064
Fe_2O_3	.574
MgO	.050
Ni	.024
Cu	90.74
Bi	0.00007
Se	0.0044
Te	0.0046
Co	.0056
MoO_3	.009
Pb	.035
As	.045
Sb	.001
Sn	.027
SO_3	1.117

It was discovered[6] in 1944 that if the copper dendrites are shattered into individual tendrils under proper conditions of drying and controlled oxidation a continuous and protective film of cuprous oxide is formed at the surface and further oxidation is stopped. The resulting particle is remarkably stable in air in contrast to the behavior of either finely divided copper or cuprous oxide alone. Presumably each protects the other. The properly formed film of cuprous oxide keeps air from the metallic copper core, and its contact with that core prevents the cuprous oxide film from oxidizing further to cupric oxide.

The Cupreous Particle

The typical particle is shaped like an Idaho potato but with many more protuberances. If it were a sphere representing the average of all particles, its diameter would be approximately 2 microns. It is made up of a metallic copper core, comprised of approximately 23,000 crystallites measuring 700Å on an edge. This core represents 80 per cent of the weight of the particle and is surrounded by a continuous and protective film of cuprous oxide. This film, amounting to 20 per cent by weight, is about 720Å thick, about 7.2 per cent of the radius of the particle.

A typical distribution of particle sizes is shown in Figure 41-1. Less than 5 per cent by weight of the powder consists of particles greater than

10 microns in diameter and the bulk of it is smaller than 5 microns. Surface measurements employing low-temperature nitrogen absorption[7] indicate that the particles do not contain capillaries, and that the total surface area is in the range between 1.2 and 3.4 square meters per gram. Comparison of this value with calculations based upon data obtained by sedimentation methods (which assume the particles to be spheres) indicate that the particles have more than three times the surface area that they would have if spheres.

The specific gravity is 7.37 grams per milliliter and bulk density is 18.5 pounds per gallon. It disperses well in water and organic liquids. The solubility in distilled water (exposed to air) is 7.5×10^{-4} grams per 100 milliliters.

This cupreous powder is obviously unsatisfactory for most metallurgical purposes because of the cuprous oxide film on the particles and because of the contamination.

In contrast to the high purity required for metal compacts, however, *copper is required for a variety of uses that might be termed "chemical"* because they depend upon solution of "cuprous" copper at a steady and sustained rate and preferably from a material that can be dispersed on or throughout the environment with which it is to react.

For such purposes the associated materials are not objectionable. On the contrary, they are often actually helpful because of their effect upon

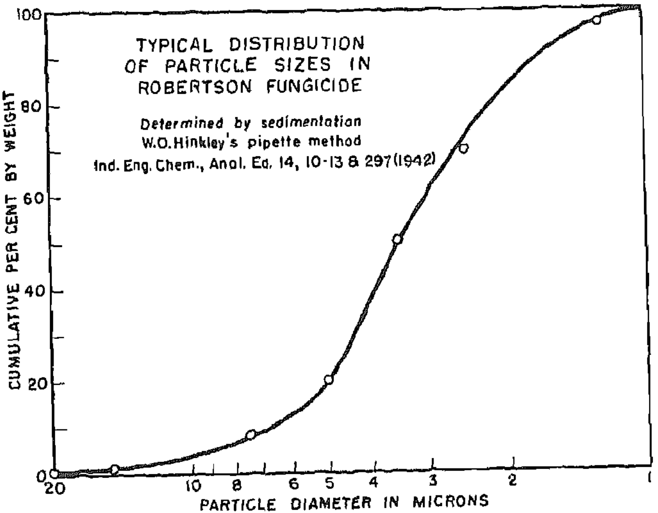

FIGURE 41-1.

the physical characteristics of the powder and perhaps because of the synergistic or promoting effect of trace amounts of other metals.

SOME TYPICAL USES AND THE REQUIREMENTS PECULIAR TO THEM

Antifouling Pigment

Copper has been employed to prevent the fouling of ship bottoms since the British Admiralty recognized the effectiveness of copper sheathing on H.M.S. Alarm, in 1763[8]. The commonly used antifouling paints contain copper or mercury compounds that are poisonous to marine organisms and prevent their attachment to ship bottoms. To be toxic they must dissolve in sea water at a rate sufficient to maintain a toxic environment adjacent to the hull. In the case of cuprous oxide and "copper pigment" the minimum adequate leaching rate appears to be about 10 micrograms[9] per square centimeter per day. A lower concentration fails to prevent fouling and, on the other hand, too soluble a toxic will be washed away and fail to sustain the necessary concentration over the years required of it.

A satisfactory leaching rate therefore is the first requirement. In addition, the pigment must disperse well in the paint and not detract from its film integrity. It must not be too reactive with the other constituents of the paint nor should it appreciably accelerate corrosion of the steel hull[10]. For this reason a cuprous oxide film amounting to a minimum of 6 per cent by weight is required of "copper pigment." Other requirements of the Navy's specification for "Copper Pigment," Mil-C$_3$15166 (June, 1950) are as follows:

	Minimum Per Cent	Maximum Per Cent
Total of metallic copper and cuprous oxide	86	
Chlorides (Cl)		0.2
Sulfate (SO_4)		2.5
Acetone-soluble matter		.5
Water		.5
Metals other than copper		1.0
Residue on 326-mesh sieve		1.0
Cuprous oxide	6.0	

Agricultural Fungicides

Copper compounds have been employed as agricultural fungicides since copper sulfate in *Bordeaux mixture* proved so spectacularly effective in 1882[11]. For this purpose it is required that "cuprous" copper be released at a rate sufficient to control fungi without appreciable harm to the host plant. The solubility of copper from most copper fungicides under conditions simulating leaf exposure lies within the range 4×10^{-3}

and 4×10^{-6} grams per 100 ml of water. The effectiveness of such sparingly soluble copper compounds indicates that either this small amount is lethal to fungi or some natural agency such as the exudate from fungi[12] dissolves additional amounts of copper.

In addition to possessing a satisfactory rate of solution, a fungicide must have certain physical characteristics as a powder. It must disperse uniformly over large areas, remain on the leaf for a reasonable period in spite of the weather, and contain a sufficient number of particles per pound to provide adequately close spacing on the leaf. This requires that the powder have extremely fine particle size and that it handle well in water suspensions or when dispersed in dust formulations. Cupreous powder, having a particle-size distribution such as shown in Figure 41-1, contains approximately 14.7 trillion particles per pound. Application of this powder at the rate of 2 pounds per acre provides over 4 million particles per square inch, spaced not more than 0.0005 inch apart. Its surface area will be well over 10 million square centimeters, ample surface for the release of cuprous ions to moisture films.

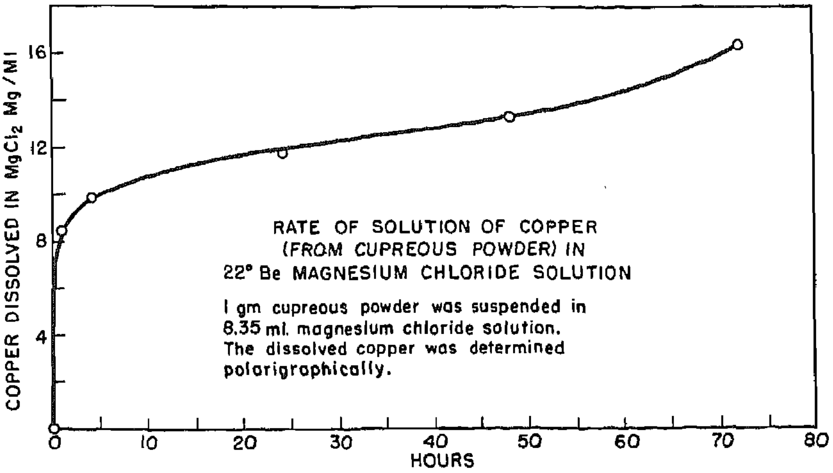

FIGURE 41-2.

Both the metallic copper core and the cuprous oxide film are classed as "active ingredient" by the U. S. Department of Agriculture[13]. Dosage is based on the total copper content. For most purposes the cupreous powder is used at the rate of 2 pounds per hundred gallons and applied at the rate of 100 to 125 gallons per acre. In dust formulations 6.6 to 7.7 pounds of the cupreous powder are used per 100 pounds of the dust, which is applied at the rate of approximately 40 pounds per acre.

Catalysts

Copper compounds are employed as catalysts in more types of reactions than those of any other metal. The requirements peculiar to each use are varied and make generalizations difficult, except that the powder should possess a large surface area of the proper degree of oxidation. The effectiveness of the cupreous powder as a catalyst in certain processes may be due to some extent to the "promoter" effect of the associated metals in trace amounts.

Cements

In the presence of air, chloride salts convert the cupreous powder to cupric oxychloride[14] in a manner similar to the formation of blue-green patina on copper roofs. The cupreous powder, because of its large surface and its degree of oxidation, dissolves slowly in the chloride solution, and, in the presence of air, is reprecipitated as the insoluble, voluminous basic chloride. This is of benefit to certain cements as follows:

Additions to portland-cement compositions react with chlorides that are present either as a result of exposure to sea water or certain ground waters, or present in the original ingredients (as calcium chloride). The formation of this new insoluble phase in the hardened cement gel effectively plugs it and, in the case of exposure to sea water or aggressive ground waters, improves its resistance to disintegration[14a].

In the case of magnesium oxychloride cements the cupreous powder slowly goes into solution to reprecipitate as basic cupric chloride throughout the hardened cement gel[15]. In doing this it performs the further benefit of scavenging the excess magnesium chloride which is inevitably present in these cements to the detriment of their stability. The result is to confer water durability[16] and to prevent expansion in the latter stages of hardening. Copper is the only metal that performs in this manner, for although other metals form insoluble voluminous basic chlorides, they react too quickly.

Because of the copper compounds in these cements, their surfaces discourage the growth of bacteria and fungi[17, 18, 19]. This has introduced the possibility of "concurrent sanitization."[18] They are also repellent to cockroaches[20].

Cupreous powder intended for this use must have ample surface area, preferably 1.2 or more square meters per gram. It must be free from cupric oxide and preferably contain no more than 20 per cent cuprous oxide.

ANALYTICAL PROCEDURES

Usual analytical procedures are employed to establish the identity and amount of each constituent that is significant to the performance of the cupreous powder, including "total copper." However, it is difficult, chemically, to distinguish between metallic copper, cuprous oxide, and cupric oxide in a mixture. Fortunately, this system is well adapted to x-ray methods. Once it is established by x-ray methods that cupric oxide is absent in detectable amounts, a simplified chemical procedure can be used to determine the per cent of cuprous oxide. The results obtained by the two methods have differed by not more than 4 per cent and half of the time are within 1 per cent.

Based on the selective solubility of cuprous oxide in aqueous ammonia, the principle of the Hurd and Clarke[25] method, a rapid control procedure for determination of cuprous oxide was developed by Miller and Gales[26]. The sample of oxidized copper powder was treated with aqueous ammonia in the presence of a carbon dioxide atmosphere. The reaction was performed directly in an Allihn filtering tube (five porosity fritted disk) and a reaction time of three minutes was used. The solution was drawn through the filter by suction and caught in a filter flask containing an excess of ferric ammonium sulfate solution. The reduced iron was titrated with standard potassium dichromate indicator using diphenylamine indicator.

Information regarding particle-size distribution below 325 mesh can be obtained by a variety of methods[21], each having both advantages and limitations. Since all are described in ample detail in the literature, it may suffice to observe that microscopic methods provide the most reliable information about particle shape and peculiarities in the distribution of particle sizes. Methods based on sedimentation are best suited for quantitative data on size distribution. Air permeability measurements provide a quick and reproducible test for production control and when correlated with occasional sedimentation tests and performance data acquire significance.

Surface area can be measured directly by low-temperature absorption of nitrogen[22].

X-ray Diffraction Analysis of Copper-Cuprous Oxide-Cupric Oxide Mixtures

Binary mixtures of finely dispersed copper and cuprous oxide can be analyzed quantitatively with an x-ray spectrometer using Cu$K\alpha$ radiation. Mixtures of known composition are prepared, and the areas above background of the 2.08A copper line (A_{Cu}) and the 2.45A cuprous oxide line (A_{Cu_2O}) are determined. A calibration curve of per cent Cu_2O as a function of A_{Cu_2O}/A_{Cu} is then drawn, from which the composition of "unknown" mixtures can be read. The presence of substantial amounts of CuO requires that a more complicated procedure be employed for the analysis of Cu and Cu_2O. However, concentrations smaller than 10 per cent can be satisfactorily allowed for by a photographic method. A Debye-Scherrer pattern of the specimen is prepared and the presence of CuO established by noting the appearance of the two sensitive lines at 2.51 and 2.31A. The intensity of the 2.51A line (I_{CuO}) is placed on a numerical basis by comparison with a special scale of spots of graded intensity. To a sufficient approximation the percentage of CuO is then given by $100(I_{\mathrm{CuO}})/(I_{\mathrm{CuO}})$., (I_{CuO}). being the intensity of the 2.51A line of a reference sample of pure CuO measured in the same way.

Any pronounced variations in line breadth from one sample to another are due to crystallite size differences. If D is the mean dimension of the crystallites constituting a powder, λ the wavelength of the x-rays, and θ the Bragg angle(the breadth of a line at half-maximum intensity, excluding instrumental effects, is given by[23]

$$B = \frac{K\lambda}{D \cos \theta}.$$

For ordinary work the constant K is assigned a value of unity. In applying the formula, allowance must be made by established methods for that part of the observed breadth resulting from instrumental factors[24].

The term *crystallite size* is not synonymous with *particle size.* Although occasionally each particle of a powder may actually be a single crystal or crystal fragment, more commonly a particle comprises a large number of crystallites. For example, the electron or optical microscope may disclose dendritic copper growths many microns in length and 1 micron in diameter, whereas the line breadths indicate that the mean crystallite dimension is about 0.07 micron. In this instance each dendrite must be composed of several thousand copper crystallites.

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Chapter 42

Copper in Organic Chemistry

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Copper and its inorganic salts occupy a prominent place in organic chemistry. They find important use as catalysts in the Gattermann, Sandmeyer, and Pschorr syntheses as well as in certain oxidation and reduction reactions. They form important complexes with 8-hydroxyquinoline, phthalocyanine, and other organic compounds. Copper itself is used in the Ullmann biaryl synthesis.

It is surprising, then, despite the broad diversity of reactions shown by copper and its salts, that organometallic compounds of copper (with the possible exception of copper acetylide) have not attained real importance. This is undoubtedly due to the difficulty of preparing such compounds and the fact that they are thermally unstable.

ORGANOMETALLIC COPPER COMPOUNDS

The term "organometallic" is used here with reference to those compounds in which copper is bonded directly to a carbon atom. Thus molecular complexes, co-ordination compounds, copper-oxygen bonded compounds, etc., are not considered under this heading.

Preparation

The most obvious approach to the preparation of a copper organometallic compound would involve the reaction of a copper halide with a more active organometallic. This approach was tried as early as 1859 when Buckton[1] reported that diethylzinc reacted vigorously with cuprous chloride to form free copper. But in his own words: "Eine Verbindung von Kupfer mit Aethyl liefs sich nicht erhalten." In 1861 Wanklyn and Carius[2] reported that both cupric iodide and cupric chloride react with diethylzinc to form copper and a mixture of hydrocarbon gases (ethane, ethylene, butane). Again no organic copper compound was detected. In 1864 Frankland and Duppa[3] heated diethylmercury with copper filings and got no reaction at 100°C. After heating the mixture at 150°C for 5 to 6 hours, a mild reaction occurred which formed amalgamated copper and a gas. The authors assumed that the gas arose from the thermal decomposition of diethylmercury rather than any reaction involving the copper.

The reaction of the Grignard reagent with copper halides has been investigated quite extensively. Krizewsky and Turner[4] reported in 1919 that when either anhydrous cupric chloride or anhydrous cupric sulfate is treated with the phenyl Grignard reagent, good yields of biphenyl can be obtained with no evidence for organocopper formation. Numerous other workers at about this same time investigated the reaction of the Grignard reagent with inorganic salts like $CuCl_2$, $HgBr_2$, $FeCl_3$, and $FeBr_3$[5]. In all cases they did not detect the intermediate organometallic compound but isolated instead excellent yields of coupling product. Much of this early work can be explained on the basis of a free radical mechanism as proposed by Kharasch[6]. In 1923 Reich[7] finally succeeded in preparing the first organocopper compound. He obtained phenylcopper by the action of cuprous iodide on phenylmagnesium bromide in ether.

$$\mathrm{CuI} + \mathrm{PhMgBr} \xrightarrow{\text{ether}} \mathrm{PhCu} + \mathrm{MgBr_2} + \mathrm{MgI_2}$$

Unfortunately the phenylcopper thus obtained was so unstable and impure that its analysis was only approximate (theoretical 45 per cent Cu; found 41 to 43 per cent). The chemistry of this substance as reported by Reich, however, would seem to leave little doubt that he actually had obtained at least some phenylcopper by this method.

In 1936 Gilman and Straley[8] attempted to repeat the preparation of phenylcopper as described by Reich. Their conclusion was that this method was inferior to that employing phenylmagnesium iodide rather than phenylmagnesium bromide. In the latter case they obtained a highly impure product which gave a prompt Color Test I[9]. Since phenylcopper gives a negative color test, this would indicate that the impurity, at least in part, was unreacted phenylmagnesium bromide.

p-Anisylcopper[8] was also prepared by these workers from *p*-anisylmagnesium bromide and cuprous iodide in 51 per cent yield. This product also gave a positive Color Test I, but it was the opinion of the authors that this, too, was caused by an impurity.

Whaley and Starkey[10] reported a seemingly attractive method for synthesizing arylcopper compounds in 1943. This involved the decomposition of diazonium borofluorides in the presence of copper powder in a hydrocarbon solvent. These authors suggested that phenyldiazonium borofluoride decomposes as follows in either dry benzene or toluene:

$$PhN_2BF_4 + 2Cu \xrightarrow{70\text{-}80^\circ} PhCu + N_2 + CuF + BF_3$$

The following copper compounds were reportedly prepared by this method (10*a,b*). The figures in parentheses represent the yields reported. C_6H_5Cu (4 to 8 per cent); *o*-$NO_2C_6H_4Cu$; *m*-$NO_2C_6H_4Cu$ (34 per cent); *p*-$NO_2C_6H_4Cu$ (30 to 35 per cent); *p*-$CH_3C_6H_4Cu$; *p*-$NH_2SO_2C_6H_4Cu$ (15 to 20 per cent).

Recently considerable doubt has been cast upon some of the conclusions of Whaley and Starkey through the later work of Warf[10c], who claims that copper powder reacts with phenyldiazonium borofluoride in the following fashion:

$$2PhN_2BF_4 + 2Cu \rightarrow 2CuBF_4 + 2N_2 + Ph\text{-}Ph$$

It is to be noted that this latest view discounts the formation of organocopper compounds entirely in this reaction.

It is highly likely that phenylcopper has fleeting existence in the cleavage of tetraphenyllead with copper nitrate trihydrate.

$$(Ph_4)_4Pb + Cu(NO_3)_2 \cdot 3H_2O \xrightarrow{C_2H_5OH} (Ph)_3PbNO_3 + [PhCu]$$

Thus Gilman and Woods[11] were able to isolate 87 per cent *m*-dinitrobenzene (prepared to derivatize the benzene), 69 to 76 per cent triphenyllead nitrate, and a trace of biphenyl from the reaction mixture. It is highly likely that the benzene was formed by the solvolysis of the intermediate phenylcopper.

Of the aliphatic copper derivatives only methyl- and ethyl-copper have been reported. Methylcopper can be prepared in 57 per cent yield by treating a solution of methyllithium in anhydrous ether with a suspension of cuprous iodide in ether cooled to -15°[11].

$$MeLi + CuI \rightarrow MeCu + LiI$$

It can also be prepared by cleaving tetramethyllead in alcohol at -70° with copper nitrate trihydrate.

$$Me_4Pb + Cu(NO_3)_2 \cdot 3H_2O \xrightarrow{\text{alcohol}} [MeCu] + Me_3PbNO_3$$

Thus Gilman and Woods[11] report the formation of 21 per cent methane, 75 per cent ethane, and 71 per cent trimethyllead iodide (used to derivatize trimethyllead nitrate) from this reaction. Treatment of the reaction mixture with benzoyl chloride led to the isolation of some acetophenone, which tended to establish the presence of the methylcopper. Bawn and Whitby[12] explain the formation of methane and ethane in these reactions by assuming that part of the methylcopper forms methyl radicals which dimerize to ethane, while the rest reacts with the ethanol solvent to form methane.

Reich[7] attempted to prepare ethylcopper by treating ethylmagnesium bromide with cuprous iodide in ether. He concluded that ethylcopper was thermally unstable even at $-18°$. This conclusion was corroborated by Gilman and Straley[8], who demonstrated that at $-18°$ ethylcopper evolved a gas and at this temperature could not be derivatized very successfully. They were able to obtain at least a 22 per cent yield of the organometallic compound by treating cuprous iodide with ethylmagnesium iodide in a dry ice-ether bath. It is also highly likely that ethylcopper is formed at least transiently in the cleavage of tetraethyllead with copper nitrate trihydrate[11]. The reaction undoubtedly proceeds in much the same manner as indicated above for the methyl derivative.

Physical Properties

Phenylcopper was described by Reich[7] as a white solid insoluble in alcohol and carbon disulfide. It is slightly soluble in chloroform, carbon tetrachloride, ethyl bromide, bromobenzene, and benzene. It is soluble in pyridine (forming a complex), benzyl cyanide, and benzaldehyde. The physical characteristics of methyl- and ethyl-copper have not been reported.

Chemical Properties

The following equations summarize the chemistry of organocopper compounds thus far reported. The number in parentheses following each equation refers to the literature reference in which the reaction is reported.

(1) $\text{PhCu} \xrightarrow[\text{absence of air}]{\text{refluxing } C_6H_6} \text{Cu} + \text{Ph-Ph}$ (7)

(2) $\text{PhCu} \xrightarrow{80°}$ explodes, forming Cu + Ph-Ph (7)

(3) $\text{PhCu} + H_2O \rightarrow \text{Ph-H} + Cu_2O$ (7)

(4) $\text{PhCu} + H_2O \rightarrow \text{Ph-H(trace-36\%)} + \text{Ph-Ph (25-56\%)}$ (8)

(5) $\text{PhCu} + \text{conc. } HNO_3 \rightarrow$ explodes, forming $\text{Ph-}NO_2$ (7)

(6) $\text{PhCu} + CH_3COCl \xrightarrow{\text{ether}} PhCOCH_3 \text{ (56\%)}$ (8)

(7) $\text{PhCu} + \text{PhCOCl} \xrightarrow{\text{ether}} \text{PhCOPh (55\%)}$ (8)

(8) $\text{PhCu} + BrCH_2\text{–}CH{=}CH_2 \xrightarrow{\text{ether}} \text{Ph–}CH_2\text{–}CH{=}CH_2 \text{ (31\%)}$ (8)

(9) $\text{PhCu} + \text{PhNCO} \xrightarrow{\text{ether}} \text{PhNHCOPh (14\%)}$ (8)

(10) $\mathrm{PhCu} + \mathrm{PhCHO} \xrightarrow{\text{ether}} \mathrm{PhCHOHPh}\ (24\%) + \text{Ph-Ph}\ (18\%)$ (8)

(11) $\mathrm{PhCu} + \mathrm{PhCN} \xrightarrow[\text{24 hr}]{\text{ether}} \text{no reaction}$ (8)

(12) $\mathrm{PhCu} + \mathrm{PhCO_2Et} \xrightarrow[\text{24 hr}]{\text{ether}} \text{no reaction}$ (8)

(13) $\mathrm{PhCu}\ (6.0\ \mathrm{g}) + n\text{-}\mathrm{C_4H_9Br}\ (4.0\ \mathrm{g}) \rightarrow n\text{-}\mathrm{C_4H_9Br}\ (2.1\ \mathrm{g}) + \text{Ph-Ph}\ (63\%)$ (8)

(14) $\mathrm{PhCu}\ (4.6\ \mathrm{g}) + \mathrm{PhCOPh}\ (6.0\ \mathrm{g}) \rightarrow \mathrm{PhCOPh}\ (4.2\ \mathrm{g}) + \text{Ph-Ph}\ (36\%)$ (8)

(15) PhCu + Michler's ketone (Color Test I) → no reaction (8) (10a)

(16) $p\text{-}\mathrm{CH_3OC_6H_4Cu} + \mathrm{CH_3COCl} \xrightarrow{\text{ether}} p\text{-}\mathrm{CH_3OC_6H_4COCH_3}\ (52\%)$ (8)

(17) $p\text{-}\mathrm{CH_3C_6H_4Cu} + \mathrm{CH_3COCl} \xrightarrow{\text{no solvent}} (p\text{-}\mathrm{CH_3OC_6H_4})_2\ (62\%)$ (8)

(18) $\text{p-}\mathrm{CH_3OC_6H_4Cu} + \left\{\begin{matrix}\mathrm{PhCN}\\ \mathrm{CH_3CO_2Et}\\ \mathrm{PhCO_2Et}\\ \mathrm{PhCOPh}\end{matrix}\right. \rightarrow \text{all no reaction}$ (8)

(19) $\mathrm{CH_3Cu} + \mathrm{PhCOCl} \rightarrow \mathrm{PhCOCH_3}\ (57\%)$ (11)

(20) $\mathrm{C_2H_5Cu} + \mathrm{PhCOCl} \rightarrow \mathrm{PhCOC_2H_5}\ (22\%)$ (8)

In reactions (3) and (4) it is to be noted that there is a discrepancy in the reporting of biphenyl as a product. It would seem likely that this substance is actually formed during the hydrolysis, however, since it occurs in too large a quantity (25 to 56 per cent) to be accounted for merely as a by-product in the preparation of the Grignard reagent.

It has been reported, but without experimental justification, that organocopper compounds do not undergo carbonation with solid CO_2[10a]. It is possible that they do form complexes with dioxane and ethyl ether which cause their precipitation from solution. The low analytical values for phenylcopper reported by Reich[7] may have been due in part to the presence of such onium complexes. Molecular complexes with inorganic cuprous compounds are well known[13, 14, 15].

Relative Reactivities[8]

Purely on the basis of comparison it is obvious that RCu compounds are more reactive than R_2Hg types and less reactive than R_2Zn compounds. Also, the order of decreasing activity in Group IB follows the generalizations made previously[16], namely, RCu > RAg > RAu. The evidence for these statements is derived from observations like the following. R_2Zn but not RCu compounds react with benzonitrile, whereas RCu but not R_2Hg compounds react with benzaldehyde.

On the basis of yields, the RCu compounds are more reactive than RAg types. Thus phenylsilver gives lower yields of acetophenone (from acetyl chloride) and benzanilide (from phenylisocyanate) than does phenylcopper under corresponding conditions. Trimethylgold[17] does not react with benzoyl chloride at temperatures up to −20°, whereas under essentially the same conditions methylcopper reacts with benzoyl chloride to form acetophenone.

Thermal Stability of Organocopper Compounds. In general, *p*-anisylcopper is slightly more thermally stable than phenylcopper, which in turn is much more stable than ethylcopper. At room temperature, out of contact with air, phenylcopper turns black in 48 hours, but the decomposition is never vigorous. It appears that the compound detonates only when heated. Ethylcopper decomposes in ether even at −18° and in so doing readily evolves a gas.

Copper Acetylide

In one sense copper acetylide is a typical organometallic compound in that it possesses a Cu-C bond. It does not, however, have the usual chemistry which is associated with organocopper compounds. Thus it does not react with water or carbonyl compounds and is quite explosive. Its color and composition seem to vary widely depending upon the conditions for its formation. Despite its peculiarities it is perhaps *the* most important organocopper compound in use at the moment. Reppe and coworkers[18] have recently disclosed a wide usage for this substance as a catalyst in vinylation and ethynylation reactions of acetylene.

Preparation. Red, explosive cuprous acetylide was first prepared by Quet[19] in 1858 before its exact composition was known. It was made by passing "pyrolytic gases" through an ammoniacal cuprous chloride solution. Boettger[20] regenerated a gas from this precipitate by treating it with hydrochloric acid. Berthelot[21] named the gas acetylene. Several workers attempted to deduce the structure of cuprous acetylide from analytical data[22, 23, 24]. It first appeared that the apparently water-free precipitate had the approximate composition $Cu_2C_2.H_2O$[24]. It was also found that after drying it over sulfuric acid[25] or calcium chloride[24] the composition approached Cu_2C_2.

Copper acetylide is perhaps most easily prepared by passing acetylene through a fairly strong ammoniacal cuprous chloride solution. As the following table[26] clearly indicates, the composition of the product thus obtained varies considerably depending upon the alkalinity of the solution. (Alkalinity decreases from 1 to 4; 5 is weakly acid).

No.	Color	Ratio (C/Cu)	Properties
1	Scarlet	1.2	Exploded on striking
2	Scarlet	0.94	
3	Scarlet	1.13	
4	Maroon	1.10	
5	Black, amorphous	1.49	No effect on striking

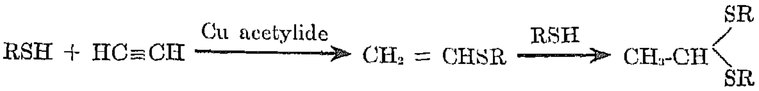
It has been suggested that cuprous acetylide can be best prepared in the pure state in the presence of reducing agents like hydroxylamine, sulfur dioxide, hydrazine sulfate, or formaldehyde. On the other hand, cuprous acetylide thus prepared is found to be far less explosive than the material prepared in the absence of reducing agent. This obviously points to a difference in composition between the two products. The explanation has been offered that the less explosive product is actually an addition complex between the copper acetylide and the reducing agent. The fact that the C/Cu ratio of the product obtained from the formaldehyde solution is 4 lends some support to this observation[26].

Copper acetylides can also be formed by treating solutions of *cupric* chloride, sulfate, borate, tartrate, phosphate, and acetate with acetylene[26]. Again the composition of the product is greatly influenced by the reaction conditions which are used. Unfortunately the composition of very few of the copper acetylides thus far prepared actually has been determined. A great deal of research must be done in this field before generalizations can be made.

Undoubtedly much of the complexity of structure evidenced by the copper acetylides is caused by the great ease with which acetylene forms addition complexes with cuprous salts. Thus Berthelot[27] reported the formation of a precipitate by the action of acetylene on neutral aqueous solutions of cuprous halides. He erroneously regarded this precipitate as a complex substitution product of acetylene. Chevastelon[28] obtained colorless crystals of an addition product with the approximate composition $C_2H_2.Cu_2Cl_2$. Manchot[13, 14] studied exhaustively the absorption of acetylene in acidified aqueous cuprous chloride solutions. In addition to $C_2H_2.Cu_2Cl_2$ previously reported he also prepared a crystalline material of the composition $C_2H_2.CuCl$. Hofmann and Kuespert[29] have claimed, without confirmation, the formation of $C_2H_2.3Cu_2Cl_2$.

It has been found that cuprous chloride addition compounds of a few monosubstituted acetylenes lose hydrogen chloride and are converted to cuprous acetylides on treatment with water or ammonia. The generalization can perhaps be made that in neutral, slightly alkaline, or very slightly acid solutions, cuprous salts give precipitates with acetylene intermediate in composition between cuprous acetylides, formed in distinctly alkaline solutions, and the addition products formed in strongly acid solutions (24*b*, p. 61).

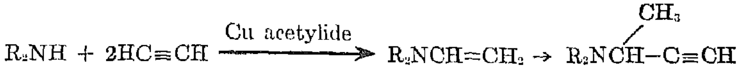
Uses. Copper acetylide probably finds its greatest use at present as a catalyst in vinylation and ethynylation reactions of acetylene. Thus acetylene reacts with mercaptans in the presence of copper acetylide to form either vinyl sulfides or thioacetals (vinylation)[18].



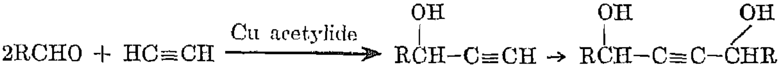
$$RSH + HC{\equiv}CH \xrightarrow{\text{Cu acetylide}} CH_2 = CHSR \xrightarrow{RSH} CH_3\text{-}CH(SR)_2$$

The following reactions[18] which are catalyzed by copper acetylide fall into the category of ethynylations wherein the triple bond of acetylene is maintained throughout.

$$2(CH_3)_2NCH_2OH + HC{\equiv}CH \xrightarrow{\text{Cu acetylide}} (CH_3)_2NCH_2{-}C{\equiv}C{-}H \rightarrow (CH_3)_2NCH_2{-}C{\equiv}C{-}CH_2N(CH_3)_2$$



$$R_2NH + 2HC{\equiv}CH \xrightarrow{\text{Cu acetylide}} R_2NCH{=}CH_2 \rightarrow R_2NCH(CH_3){-}C{\equiv}CH$$



$$2RCHO + HC{\equiv}CH \xrightarrow{\text{Cu acetylide}} RCH(OH){-}C{\equiv}CH \rightarrow RCH(OH){-}C{\equiv}C{-}CH(OH)R$$

Since all of these are pressure reactions, one might question the wisdom of carrying them out with dangerous copper acetylide under such conditions. Reppe, however, claims that the active catalyst is not $Cu_2C_2.H_2O$ but rather its far less dangerous addition compounds with acetylene like $C_2H_2.H_2O.C_2H_2$ and $Cu_2C_2.H_2O.C_6H_6$. The catalyst must be prepared so that it is highly reactive and wear-resistant. This is done as follows[18b]:

Silicic acid is soaked several times in a strong nitric acid solution of copper nitrate and bismuth nitrate (Cu:Bi = 4:1) until the metal content is equal to 12 per cent copper and 2 per cent bismuth. The silicic acid is in the form of rods 4 to 6 mm in diameter and 6 to 8 mm long stabilized by glowing at a temperature of 800°C. The soaked catalyst is heated to 450°C. The material is packed into reaction towers and then "developed." This is done by circulating dilute formaldehyde (5 to 20 per cent) at 70°C in the presence of acetylene through the mass for 12 hours. Toward the end of the development period the temperature is raised to 90°C. The catalyst is then ready to function.

The red color of copper acetylide has been used as a qualitative test for the detection of acetylene. However, since this color darkens (especially in a basic medium) due to air oxidation, a reducing agent like hydroxylamine is necessary to preserve the red color. A very sensitive reagent for acetylene consists of an ammoniacal cuprous chloride solution containing gelatin as a protective colloid. This keeps the red acetylide in a fine state of division so that its color can be readily observed at great dilution[30].

Copper acetylide is too sensitive to shock to be of practical value as an explosive. It is of interest that explosions involving this material produce copper and carbon but no gaseous products.

Conclusion

The above discussion brings up to date the organometallic chemistry of copper. Certain reactions may well proceed by way of an organocopper intermediate, but in no case has this been definitely established. Thus in the "direct process" for the preparation of methylchlorosilanes[31] it has been suggested that methylcopper has a transient existence of about 0.003 second.

$$2Cu + CH_3Cl \rightarrow CuCH_3 + CuCl$$

$$CuCH_3 \xrightarrow{300^\circ} Cu\cdot + CH_3\cdot$$

Certainly the temperature of 300°C at which the reaction is carried out would insure that the thermally unstable methylcopper would have only fleeting existence.

It has also been suggested that organic copper compounds are formed as intermediates in the Gattermann reaction[10a], in certain modifications of the Bart synthesis[32], and in the replacement of a diazo group by hydrogen[33]. It must be emphasized, however, that these reactions are merely suggestive of organocopper intermediates but that little evidence is at hand to substantiate this.

Copper-Chromium Oxide Hydrogenation Catalyst

The copper-chromium oxide combination and nickel are probably the two most useful hydrogenation catalysts now available, since they supplement each other so admirably.

Preparation[35, 36]

There are several methods available for the preparation of the copper-chromium oxide catalyst. Perhaps the most active preparation is obtained by adding cupric nitrate trihydrate, calcium nitrate, and ammonium dichromate to a 28 per cent ammonium hydroxide solution. The precipitate which forms is filtered off, dried, and decomposed in a casserole over an open flame. After the evolution of gases ceases, the entire mass turns black. It is then cooled, leached with 10 per cent acetic acid, filtered, washed with water, and dried in an oven at 125°C. The product thus prepared is stable indefinitely.

Composition of Copper-Chromium Oxide

The catalyst probably has the formula $CuCr_2O_4$[37], although this has not been definitely established. Its black color suggests that the copper is in the divalent state. Under some conditions the catalyst is reduced to reddish colored compounds. This reduction to the monovalent or elemental state occurs, for example, at 360°C when ethanol is passed over the catalyst. It is possible, however, to effect this reduction at temperatures as low as 150 to 175°C in the presence of more easily oxidized compounds. The reddish copper compounds thus obtained are rather inactive as hydrogen catalysts.

It has been found advantageous to have barium, calcium, or magnesium compounds present in the catalyst to retard or inhibit its reduction. It is for this reason that the calcium nitrate was added in the preparation described above. The real catalyst in the combination is probably copper oxide stabilized by the chromium oxide against reduction. Hence any method that produces cupric oxide in combination with a stabilizing substance like chromium oxide may give a good catalyst.

Scope of the Copper-Chromium Oxide Catalyst

A large number of oxides such as those of zinc, nickel, copper, chromium, and molybdenum are catalysts for hydrogenations, but they have a disadvantage in that they require relatively high temperatures (300 to 500°C). Copper-chromium oxide is active at lower temperatures (100 to 300°C), but usually requires hydrogen pressures of 100 to 300 atm. It is more resistant to poisoning than metallic catalysts, and its activity per unit weight is similar to that of platinum, palladium, and nickel.

The copper-chromium oxide catalyst is particularly recommended for the reduction of aldehydes and ketones to alcohols, of esters to alcohols, and of amides to amines. It is quite inactive for the hydrogenation of the benzenoid nucleus and may be used to hydrogenate aryl compounds without much danger of saturating the ring. Nickel, on the other hand, is not effective in reducing amides to amines and esters to alcohols. It is an excellent catalyst, however, for the hydrogenation of alkenes, benzene rings, oximes, cyanides, and nitro compounds.

This marked difference in the case of reduction of functional groups by the two catalysts can probably be accounted for on the basis of preferential absorption. Thus the copper-chromium oxide catalyst is particularly active toward groups containing oxygen, which probably indicates it is capable of adsorbing these compounds better than nickel.

COPPER AS A HYDROGENATION CATALYST

Copper itself can function as a catalyst in the hydrogenation of organic compounds. Thus nitro compounds can often be reduced over a copper catalyst to the corresponding amines in quantitative yields[38, 39]. The reduction temperatures lie a little higher than for nickel, mostly between 300 and 400°C. Thus nitrotoluenes can be reduced to nitrotoluidines at 330 to 350°; α-nitronaphthalene to α-aminonaphthalene at 330 to 350°; *p*-chloronitrobenzene to *p*-chloroaniline at 360 to 380°[40]. Nitrophenols and nitroanilines can also be reduced with copper, often in quantitative yields, to aminophenols and phenylenediamines[38, 41].

Copper may also be used in certain instances to reduce oximes and nitriles to amines, and aldehydes and ketones to alcohols.

The copper catalysts used in these reductions are readily obtained by the reduction of the oxide at 180°C. According to one report[42] copper-coated pumice is preferable to copper. This is prepared by the reduction of CuO on pumice.

Copper catalysts are far less active than nickel, but for this reason may have certain advantages. Raney nickel is so active that it may react with aromatic nitro compounds to reduce the ring as well as the nitro group. On the other hand, the action of copper is completely restricted to the nitro group so that good yields of the amine result. Further, it is less susceptible to poisons than nickel and is cheap. It can be revivified from the stale catalyst more easily than nickel[43].

The Ullmann Biaryl Synthesis[44]

The so-called "Ullmann"[45] reaction consists in the coupling of two molecules of an aromatic halide in the presence of a metal.

$$\mathrm{RX} + \mathrm{R'X} \xrightarrow{\text{metal}} \mathrm{R{-}R'} + \mathrm{MX}$$

Copper has been found to be particularly effective as the metallic coupling agent in this case. The reaction may be used to prepare both symmetrical and unsymmetrical biaryls.

The nature of the copper used in these reactions has been the subject of many discussions. Commercially available copper bronze (pulverized copper) as well as high-grade commercial copper powder are effective. Also, freshly precipitated copper (prepared from copper sulfate solution and zinc) has been used successfully.

Experimental Conditions. The reaction is usually carried out between 100 and 300°C. It is exothermic and thus often proceeds at temperatures slightly above that of the heating bath. Toward the end of the reaction the temperature begins to fall, and, at this point, more external heat is usually applied. In the case of low-boiling compounds sealed tubes are often used[46, 47].

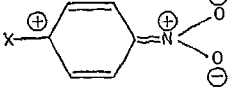
A large excess of copper is always used in the Ullmann reaction. This may be as much as five or ten times the theoretical quantity. The copper is added gradually during the course of the reaction, since if added all at once the reaction might become violently exothermic. In those cases where the reaction is otherwise violent, it is preferable to use a solvent. Nitrobenzene, toluene, and naphthalene have been used for this purpose.

Recently (communication from Dr. Nathan Kornblum)[47a] it was found that dimethyl-formamide is a good solvent for this reaction. It is particularly convenient in that it is water-soluble and can thus be removed from the reaction product quite easily. It is claimed that use of the solvent increases the yields anywhere from 15 to 30 per cent over those previously reported.

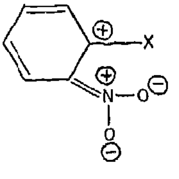
Davey and Latter[18] prepared a series of symmetrical dinitrobiphenyls by heating 2.5 grams of the halonitrobenzene to 200°C and then adding 1.5 grams of copper powder over a 20-minute period. The mixture was then heated an additional 10 minutes at 200°C and another 10 minutes at 220°C. The same compounds were also prepared by refluxing for 9 hours 5 grams of the halonitrobenzene and 3 grams of copper in 25 grams of nitrobenzene. Their results are as follows:

	Fusion (yield, per cent)	$C_6H_5NO_2$ (yield, per cent)
o-$ClC_6H_4NO_2$	40	0
o-$BrC_6H_4NO_2$	64	45
o-$IC_6H_4NO_2$	65	43
m-$ClC_6H_4NO_2$	0	0
m-$BrC_6H_4NO_2$	15	0
m-$IC_6H_4NO_2$	36	0
p-$ClC_6H_4NO_2$	0	0
p-$BrC_6H_4NO_2$	36	15
p-$IC_6H_4NO_2$	54	25

Their work clearly indicates that the yields are better when the materials are fused together than when nitrobenzene is used as a solvent. It also indicates that the iodo compounds are superior to the bromides and chlorides since the yields increase in the order RCl < RBr < RI. It also points to the fact that the activating effect of the nitro group is in the order $o > p > m$. This strengthens the notion that the resonance effects of the nitro group as well as its inductive effect are important factors. Both of these effects operate in the same direction with the nitro group and tend to make the carbon atom holding the halogen slightly positive.



The inductive effect of the nitro group, however, is most effective in the *ortho* position.

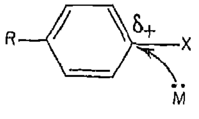


Hence in the *ortho* compound the carbon atom holding the halogen should be more positive than that in the *para* position.

Nature of the Reaction. As shown above, certain electronegative groups situated either *ortho* or *para* to the halogen have a marked activating effect on the reaction. Thus an *ortho* or *para* nitro group is very effective. This suggests that the reaction may involve an attack by a nucleophilic reagent. On the other hand, the presence of groups like the $-NH_2$, $-COOH$, and $-OH$ have an inhibiting effect on the reaction and generally result in lower yields. As a rule, these groups must first be protected by alkylation, acylation, or esterification to avoid troublesome side reactions.

Mechanism. The exact mechanism of the reaction has not been established, although it would seem that it proceeds either by way of an organocopper intermediate[8], free radicals[49, 50], or a metallic complex[50] of some sort. At the moment the free-radical mechanism probably stands in the highest favor although it has not been absolutely proved. Thus Rapson and Shuttleworth[49] showed that ArX compounds ($X = Cl, Br, I$) when treated with copper or sodium in ether consistently formed the Ar-H compounds, presumably through a reaction of the Ar radical with the ether solvent. Also, when copper bronze in a sealed tube was treated with iodobenzene and an excess of ethyl benzoate, there was obtained biphenyl-2- and -4-carboxylic acids. This was taken as evidence for the formation of phenyl radicals which attacked the ethyl benzoate in the 2- and 4-positions. It would seem, however, that if free radicals were intermediates in the Ullmann reaction several isomeric biaryls would result. This is not the case, since the only product one can isolate from the reaction contains the two aryl nuclei joined at the positions originally occupied by the halogens.

Fanta[44] has suggested that the initial and rate-determining step in the reaction might involve a nucleophilic attack by the metallic copper (M) at the activated position.

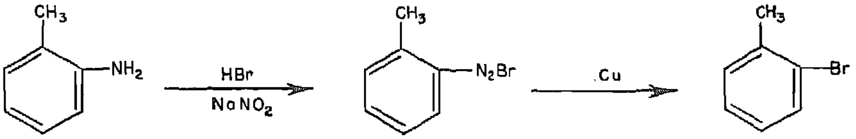


Such a picture is consistent with the experimental results of Davey and Latter[48] in that it would predict great activation by an *ortho* nitro group.

Gattermann Reaction[52]

The Gattermann reaction involves treating a diazotized amine with pure copper powder. Nitrogen is evolved, and the aryl halide is formed.

Thus *o*-bromotoluene can be prepared in 43 to 47 per cent yield starting with *o*-toluidine[53].



The so-called Sandmeyer reaction resembles the Gattermann in almost every respect except that decomposition of the diazonium salt is effected with a cuprous salt instead of copper metal.

In some respects the Gattermann reaction is superior to the Sandmeyer method. For example, only catalytic amounts of copper are required compared with a mole-for-mole equivalency in the case of the cuprous salt component. In addition, the cuprous salts are troublesome to make and cannot be stored for any length of time. Usually the Gattermann reaction may be carried out at a lower temperature than the Sandmeyer reaction, which makes it commercially more attractive. The yields in the Gattermann reaction, however, though high in some instances, never surpass those of the Sandmeyer procedure and are sometimes lower. Hence, where a choice is open, the Sandmeyer reaction is usually preferred.

There are certain cases where the cuprous salts required for the Sandmeyer reaction are not available, in which event one must resort to the Gattermann procedure[54]. Thus benzenediazonium sulfate is converted in good yields into benzenesulfinic acid by the action of sulfur dioxide and copper powder. Also, this same diazonium salt when treated with potassium cyanate and copper yields phenyl isocyanate, but only in 20 per cent yield.

Copper may also be used to catalyze the decomposition of diazoniumfluoroborates in the presence of sodium nitrite. Thus *p*-dinitrobenzene may be prepared[55].

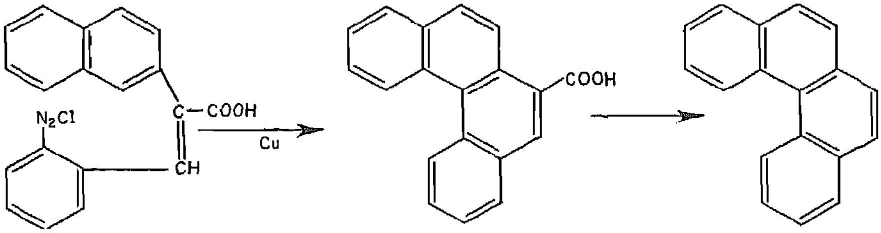
$$p\text{-}NO_2C_6H_4N_2BF_4 \xrightarrow[NaNO_2]{Cu} p\text{-}C_6H_4(NO_2)_2 + N_2 + NaBF_4$$

Perhaps the most useful application of the Gattermann procedure is the joining of two aromatic nuclei by the reaction of a diazonium salt and a hydrocarbon under the catalytic influence of copper or zinc. Thus

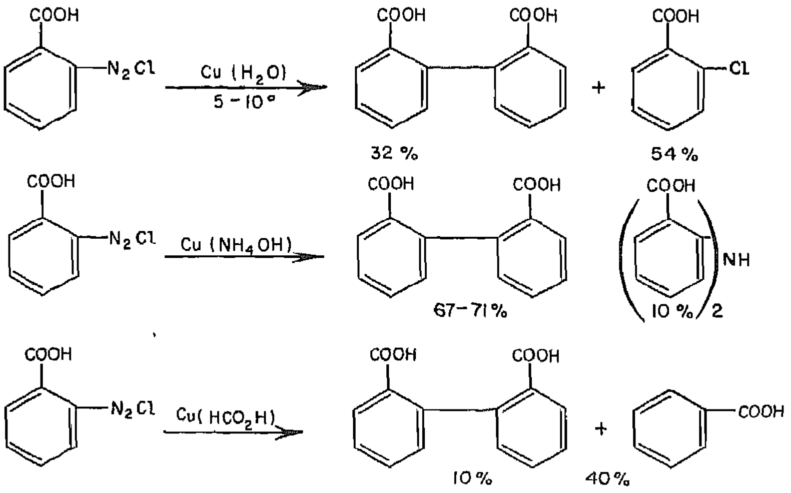
$$C_6H_5N_2Cl + C_6H_6 \xrightarrow[\text{alcohol } 30\text{-}40°]{\text{Cu(or Zn)}} C_6H_5C_6H_5 + N_2 + HCl$$

The yields are often low in this reaction, and the desired product is often contaminated with higher hydrocarbons like terphenyl, quaterphenyl, and quinquiphenyl[56]. This undoubtedly is caused by the diazonium salt reacting with biphenyl and the higher hydrocarbons rather than with benzene.

When an intramolecular coupling of a diazo compound occurs so as to close a ring, the reaction is referred to as the Pschorr synthesis. Thus 3,4-benzphenanthrene, a carcinogenic hydrocarbon, can be prepared:



A somewhat related reaction involves the preparation of symmetrical biaryls by treating substituted diazonium salts with copper powder. Thus the following reactions have been reported[57]:



Mechanism. Waters has suggested that both the Sandmeyer and Gattermann reactions are non-ionic decompositions of diazonium cations brought about by a single electron transference from a catalyst. In the initial phase an electron from the copper converts the diazonium cation to a neutral aryl radical and molecular nitrogen[50, 58]:

$$\mathrm{Cu} \rightarrow \mathrm{Cu}^{+} + e^{-}$$
$$(\mathrm{Ar{-}N{\equiv}N})^{+} + e^{-} \rightarrow \mathrm{Ar}\cdot + \mathrm{N}_2$$

In the second phase of the reaction the aryl radical reacts with the halogen anion to give an aryl halide molecule, thereby setting free an electron which can be picked up by the copper cation.

$$\mathrm{Ar}\cdot + \mathrm{Cl}^{-} \rightarrow \mathrm{ArCl} + e^{-}$$
$$\mathrm{Cu}^{+} + e^{-} \rightarrow \mathrm{Cu}$$

The formation of diaryls in the Gattermann reaction supports this mechanism to some extent, since they may result simply through the dimerization of neutral free radicals. In the final analysis, however, the above is merely a proposed mechanism and has not been definitely proved.

COPPER CATALYSIS

Copper functions as a catalyst in a variety of organic reactions, and it is not intended to infer that the few specific instances discussed above in any way exhaust the topic. Thus copper catalyzes the dehydrogenation of primary and secondary alcohols to aldehydes and ketones at elevated temperatures. Formaldehyde can be made by passing methanol over heated copper, and similarly cyclohexanol is dehydrogenated to cyclohexanone. *n*-Nonyl alcohol when passed over copper heated to 240°C forms the aldehyde in 90 per cent yield[59].

$$n\text{-}\mathrm{C_9H_{19}OH} \xrightarrow[240^\circ]{\mathrm{Cu}} (90\%)\ n\text{-}\mathrm{C_8H_{17}CHO}$$

Sabatier and Senderens[60a] also reported the following transformations:

$$n\text{-}\mathrm{C_3H_7OH} \xrightarrow[230\text{-}300^\circ]{\mathrm{Cu}} \mathrm{C_2H_5CHO}$$

$$n\text{-}\mathrm{C_4H_9OH} \xrightarrow[220\text{-}280^\circ]{\mathrm{Cu}} n\text{-}\mathrm{C_3H_7CHO}$$

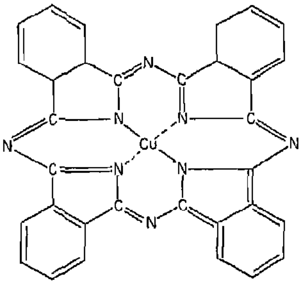
$$\mathrm{(CH_3)_2CHCH_2CH_2OH} \xrightarrow[240\text{-}300^\circ]{\mathrm{Cu}} \mathrm{(CH_3)_2CHCH_2CHO}$$

Tertiary alcohols are dehydrated to olefins by copper at 280 to 300°C almost without side reactions[60b].

COPPER COMPLEXES

Copper forms several insoluble complexes with organic compounds that have important applications. Copper phthalocyanine is a deep blue pigment used widely in printing inks, artists' colors, paints, and lacquers. When chlorinated, the compound yields an excellent green pigment. It may also be sulfonated to form a soluble compound which can be used directly as a dye.

Copper phthalocyanine can be prepared in yields as high as 90 per cent by treating copper at about 200°C with phthalonitrile. It is a very stable pigment, being unaffected by molten alkali or boiling hydrochloric acid. It has been assigned the structure



Several of the other copper complexes have important uses in analytical chemistry. Thus α-benzoinoxime, ammonium phenylnitrosohydroxylamine (cupferron), 8-hydroxyquinoline, and salicylaldoxime are a few of the compounds which form precipitates with copper salts. They can be used both as a qualitative and quantitative test for copper.

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Chapter 43

Copper in Biology

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Occurrence

It is not surprising that copper should be found widely distributed in animal and plant tissues in concentrations greatly in excess of those in which other trace metals occur, since it occurs normally in the soil to the extent of from 2.5 to 20 ppm, while in some localities 50 ppm may be found[76]. Cunningham[27] found it in the soft tissues of animals of several species, the highest concentrations being in the liver. Baroni[6] found 0.006 to 0.008 microgram in the retina and 0.003 to 0.008 microgram in the choroid of the eye of an ox, and Comar[24] has found it in the bone marrow. Many determinations have been made of the copper content of the leaves and fruit of deciduous trees[58, 84]. Values ranging from 3 to 20 ppm of dry weight were reported for leaves of Bartlett pear, peach, and cherry trees[84], for those of Kelsey plum trees[33], and for the fruit and leaves of orange and lemon trees[45]. Cockburn and Herd[23] reported that tomatoes contained from 1 to 2.5 ppm, but Monier-Williams[79] gave slightly lower values (0.25 to 1.2 ppm) for samples known to have been unsprayed. Santaolalla[96] reported the copper content of fresh alfalfa as 0.88 mg per cent and that of the dried material as 2.55 mg per cent. Clover in full bloom, with the roots excluded, contained 2.06 mg per cent[96]. Analytical data on a wide variety of foodstuffs have been presented by Lindow, Elvehjem and Peterson[66], Elvehjem and Hart[36], Hirano and Mikumo[51], King and Etzel[59], Remington and Shiver[90], McCance and Widdowson[74a], and Monier-Williams[79], among others. The amounts of natural or adventitious copper in various foods as sold throughout the world vary from 0 to 10 ppm, with certain items containing quantities greater than 100 ppm[79].

Absorption, Excretion, and Storage of Copper

The mean daily intake of copper in the food and beverages normally consumed by man has been estimated to lie between 2 and 2.65 mg by Chou and Adolph[22], Tompsett[116], Leverton[64, 65], and Kehoe, Cholak, and Story[56], although slightly lower values have been reported in Great Britain[79]. Most of the ingested copper is eliminated in the feces, the mean urinary concentration being only 0.034 mg per liter[56], and the average daily urinary output 0.25 mg[22], with a range of 0.08 to 0.48 mg[116]. Comar[24] found from 1 to 7 per cent of an orally administered dose of radioactively tagged copper and 32 per cent of an intravenously injected dose in the livers of cattle examined after a lapse of 19 to 42 hours. Similar observations have been made recently in Germany by Schubert and co-workers[102].

In human tissues, Kehoe, Cholak, and Story[56] reported the following amounts of copper, expressed as ppm of fresh tissue: liver, 7.10, kidney, 1.66, heart, 1.90, spleen, 0.85, lung, 1.10, muscle, 1.25, stomach, 1.07, intestine, 1.10, rib, 4.10, and long bone, 11.9. Herkel[50], and Schönheimer and Herkel[101], found in the liver quantities ranging from 1.33 to 13.0 ppm, but some cirrhotic livers contained it in much higher concentrations[1]. Tompsett[117] found relatively large amounts in the brain, 2.2 to 4.8 ppm, and Bodansky[15] found 3.6 to 6.8 ppm. In the ribs, Tompsett[117] found 3.7 to 4.7 ppm, in agreement with Kehoe, Cholak, and Story[56]. In the vertebrae, he found 2 to 5 ppm. Chou and Adolph[22] estimated that the entire body of an adult contains from 100 to 150 mg of copper.

Of great significance is the observation that the copper content of the livers of infants exceeds that of the livers of adults. Morrison and Nash[80] found the average content in the livers of 25 infants to be 24 ppm, which was six times their average value for the livers of seven adults. Similar observations have been made repeatedly upon the livers of animals[27, 39, 50, 75]. The spleen of new-born children is also rich in copper[93]. It has been suggested that the high values for the copper content of the livers of children may represent stores that may be drawn upon during the period when the infants are nourished chiefly on milk, which contains but little copper.

There is fairly good agreement as to the content of copper in human whole blood. Kehoe, Cholak, and Story[56] reported an average value of 0.114 mg per 100 grams, while most other investigators[10, 49, 52, 80, 94, 95, 98] have reported values within the range of 0.091 to 0.141 mg per 100 grams. Tompsett's[115] values of 0.185 to 0.229 mg per 100 ml are regarded as excessive[35]. Most investigators agree that the concentration of copper in the cells exceeds slightly that found in the plasma[37, 56, 57, 98], although a few discordant observations have been recorded[44, 115]. In disease, low values for plasma copper are rare, but high ones have been reported in acute and chronic infections, pregnancy, leukemia, malignancies, and other conditions[21]. Most of the copper in the plasma appears to be present in a blue protein, caeruloplasmin[53]. Within about five hours following the intravenous injection of a copper salt, the distribution between plasma and cells becomes normal, according to observations of Warburg and Krebs[120]. Mann and Keilin[73] have isolated from erythrocytes a blue, crystalline protein, hemocuprein, which contains 0.34 per cent copper and is present to the extent of 60 mg per 100 ml of erythrocytes. Whether it plays any role in the synthesis of hemoglobin is unknown.

The Role of Copper in the Organism

Animals. In invertebrates, copper-containing enzymes have been suggested as playing a role in rendering free-swimming forms sessile, in the formation of pigments, and, in the case of insects, in the hardening of the shells of the eggs[31].

Certain diseases of livestock are known to be due to a deficient intake of copper. The salt-lick sickness of cattle, an anemia with scouring, occurred in parts of Holland where the hay contained only 1 to 3 ppm, that of unaffected areas containing 7.5 ppm[20, 106, 107]. The blood of the affected cattle had only one-third of the normal concentration of copper. Cures were rapidly effected by removing the cattle to high-copper pastures or by drenching them with 3.5 grams of copper as sulfate. Similar illnesses have also been reported among cattle in Florida, New Zealand, and Aberdeenshire[54].

The so-called "ginginataxia" of sheep and cattle in Australia is likewise a copper-deficiency disease, the livers of affected sheep containing the metal in concentrations of only 4 to 8 ppm of dry tissue, normal values ranging from 120 to 360 ppm[11, 12, 13]. An early sign of this disease is the appearance of stringy wool, the content of copper in the hair follicles being insufficient to bring about the normal keratinization of the emerging fiber.

It is currently believed that the ingestion of excessive amounts of molybdenum leads to interference with the normal utilization of copper, and that this may account for the occurrence of copper-deficiency diseases in areas where the forage is not lacking in copper. Lambs in North Derbyshire, where the pastures were not deficient in copper, suffered from the "swayback disease," had subnormal amounts of copper in their blood, and responded to medication with copper salts[32, 105].

Experimentally, rabbits have recently been found by Smith and Ellis[109] to grow at a retarded rate, to develop anemia, and to exhibit alopecia or a loss of pigment in their hair when maintained on diets low in copper. It has also been stated by Gorter[42, 43] that the loss of pigment from the hair of black rats that occurs when they are kept on certain diets may be cured by the daily administration of 0.07 to 0.24 mg of copper. Rats can be kept in good health if their diet provides about 0.01 mg of copper daily[27].

Only a beginning has been made in the study of the mechanisms by which copper acts, but it is known that the metal is readily bound by a number of proteins and that it is a component of such respiratory enzymes as polyphenol oxidase, laccase, and ascorbic acid dehydrogenase[3, 113]. Its importance for hemopoiesis has been established beyond doubt and is deeply rooted in evolutionary history. Sea water, in which life may have had its origin, contains about 0.01 ppm[5]. The blood of snails, crabs, and lobsters has as its oxygen-carrying pigment, not the iron-containing hemoglobin of mammalian blood, but instead a blue copper-containing compound known as hemocyanin. It appears likely that when mammals appeared, and hemoglobin replaced hemocyanin, the functional relation of copper to blood formation may not have been entirely lost. The evidence for this is to be found in experiments performed upon rats with nutritional anemia, a condition which results when weanling rats are fed entirely upon milk, which is low in both copper and iron. Hart, Steenbock, Waddell, and Elvehjem[47] showed that the administration to such rats of iron alone fails to bring about recovery, or does so only slowly, while if the iron is supplemented by a small amount of copper normal blood counts are attained promptly. The minimum daily amount required in order to induce a reticulocyte response in an anemic rat may be 0.005 to 0.01 mg of copper, according to Schultze and Elvehjem[103]. The many papers, most of them confirmatory, which have since dealt with this subject have been reviewed by Elvehjem[35].

Plants. Early studies on the role of copper in plant growth attributed beneficial results to chemical stimulation[38, 65] and it was not until after Sommer's work[110] that the essential nature of copper in plant nutrition was accepted. She proved conclusively that poor yields of tomato, sunflower, and flax in water culture could be obtained by eliminating copper from the nutritive medium. Further proof of the beneficial effects of copper were soon reported for barley[68], oats[19], and tobacco[76]. Steinberg[111] and Nikitin[82] have reviewed the literature of plant diseases, particularly exanthema or dieback and reclamation disease, attributable to naturally occurring copper deficiencies.

The exact role of copper in plant physiology is still not clearly understood, but it is probable that it plays a role in those cellular processes in which the previously mentioned copper-containing enzymes participate[3]. There is also some likelihood that copper may play a role in photosynthesis, although the evidence for this is rather indirect[3]. The percentage of copper is higher in the chloroplasts than in the leaf as a whole[81], and, in spinach, the chloroplasts have a high polyphenol oxidase activity[2]. In variegated plants, green tissues are richer in copper than are chlorotic portions[99]. Okuntsov[83] has suggested that copper may act *as a stabilizer, retarding the decomposition of chlorophyll.*

Copper also appears to be a necessary nutrient for fungi[111]. The omission of copper from the medium on which Aspergillus niger was grown resulted in a significantly lowered yield and in the production of brown rather than black spores[16, 91, 92]. Metz[78] found a similar behavior on the part of 10 species of fungi. Smith[108] reported that the presence of 0.0005 per cent of copper sulfate was needed for the normal growth of *Penicillium* species, and that copper stimulates the production of citromycetin by *P. glabrum* and of citrinin by *P. imlicatum.*

Toxicity of Copper

Acute Effects. Although copper is an essential element in mammalian tissues, its presence in excess is known to be toxic. When given orally, copper sulfate, because of its local irritant properties, acts as an emetic in all species that are capable of vomiting. Cunningham[28] found that amounts of that salt up to 80 grams were not toxic when given in one dose to yearling heifers or adult cows, although a dose of 400 grams was lethal.

In man, the ingestion of a large quantity of copper sulfate has caused vomiting, gastric pain, dizziness, exhaustion, anemia, cramps, convulsions, shock, coma, and death. Symptoms attributed to damage to the nervous system and kidney have been recorded, jaundice has been observed and, in some cases, the liver has been enlarged. Deaths have been reported to have occurred following the ingestion of so little as 27 grams of the salt, while other victims have recovered after having taken much larger amounts, up to 120 grams.

Since McCance and Widdowson[74] found that the administration of BAL (dimercaptopropanol) increases from ten- to twenty-fold the urinary copper concentration, it is likely that, in part at least, the toxic action of the metal may be attributed to its entrance into combination with the thiol groups of certain enzymes. In concentrations of 10^{-4} to 10^{-3} molar, copper inhibits the glycolytic activity of muscle extracts[69].

Chronic Effects. Lower animals are said to be more sensitive to copper[79]. Toxicities for fish vary from 0.25 ppm for trout to so much as 2 ppm for other species. Most marine mollusks will not tolerate more than 0.1 to 0.2 ppm, and copper compounds are used as antifouling agents in preventing the attachment to the hulls of ships[31]. Oysters and mussels living in estuary waters liable to contamination with copper are, however, much more resistant, and copper concentrations below 0.5 to 0.6 ppm aid in their "setting"[88, 89].

A concentration of 5 ppm in water is toxic to most bacteria, but *E. coli* and the diphtheria bacillus are particularly insensitive to copper[114]. It has been claimed[77] that the bacteria living in the rumen can tolerate a concentration of 10 ppm, although their growth is inhibited by one of 25 ppm. Algae are exceptionally susceptible, their growth being stopped in the presence of 0.1 ppm[29]. Advantage is taken of this so-called oligodynamic action in freeing ponds and reservoirs from algae and other unicellular forms of life. The mechanism by which the copper acts in these low concentrations is but poorly understood[104], but a mathematical treatment of its action on *Nitella* has been given by Cook[25]. Excessive amounts of copper are toxic for fungi, and copper compounds are widely used as fungicides.

In water cultures, oats exhibited toxic effects when the concentration of copper exceeded 0.5 mg per liter, growth and the putting forth of new shoots being depressed[112]. A concentration of 2 ppm was found toxic for tomatoes[4]. Copper is toxic to turnips and spinach when present to the extent of about 200 ppm in the top 8 inches of soil[8].

Before the magnitude of the normal human dietary intake of copper had been learned, Mallory[70, 71, 72] performed a series of experiments from which he drew the conclusion that the ingestion of more than 5 or 10 mg of copper daily might cause damage to the liver. He suggested that hemochromatosis or "bronze diabetes," a rare disease, might be the result of poisoning by copper, but this disease has not been noted to occur with undue frequency among workers with copper. Other investigators, as Flinn and von Glahn[40] and Polson[87], were unable to confirm Mallory's results. On the other hand, Hall and Mackay[46], who fed rabbits a diet containing 2,000 ppm noted moderate pigmentation, chiefly in the Kupffer cells, of the livers of those that died after 21 to 29 days. The pigmentation was present when the copper content of the livers reached 750 to 1,000 ppm, and when it exceeded 1,000 ppm, cirrhosis was also noted. The nature of the hepatic damage has also been discussed by Oshima, Kamamoto, and Adachi[85]. Elevated values for the copper content of the livers of human cases of hemochromatosis have been recorded. Funk and St. Clair[41] found 140 ppm in fresh tissue, but regarded its presence as secondary to the action of an unknown etiologic agent. Oshima and Schönheimer[86] found more moderate amounts, 9.86 to 63.3 ppm. In Laennec's cirrhosis, the presence of 274 ppm has been reported and in two cases of Wilson's disease, Haurowitz[48] found 48 and 59 ppm, respectively. In experiments with copper sulfate, Santesson[97] found that when very large doses were given to rabbits over a long period, damage occurred primarily to the blood, with icterus, hematuria, hemoglobinuria, and hemorrhagic nephritis.

Early attempts were made to learn the maximum amounts of copper compounds that could be ingested daily by laboratory animals without injury[61, 62]. In 1893, Tschirch[118] concluded that a daily intake of 3.5 mg of copper oxide per kilogram of body weight caused injury to rabbits. More recently, Kiyooka[60] estimated that the maximum amount of cuprous sulfate that could be ingested daily by rabbits is of the order of 5 to 7.5 mg per kilogram. Boyden, Potter, and Elvehjem[18] reported that the presence of copper to the extent of 4,000 ppm in the diet of rats quickly led to loss of weight and death by voluntary starvation. When the diet contained 2,000 ppm, growth failed to occur, evidence of jaundice appeared, and the livers of the rats were found to contain 300 times the normal content of copper. In the livers of rats fed at 500 ppm, pathologic changes were not found although the copper content was increased 14-fold. The daily intake of copper by rats fed at this dietary level has been estimated to be 5 mg[26]. Lindow, Peterson, and Steenbock[67] found nearly 20 times the normal concentration of copper in the livers of rats fed daily for seven weeks 5 mg of copper as sulfate in addition to the 3.3 mg normally present in their food. Datta[30] found the growth of rats affected by a daily intake of from 6 to 9 mg of copper. In the opinion of the Wisconsin investigators[18] copper becomes a toxicant at some dietary level between 500 and 1,000 ppm. However, Cunningham[27], in a 22-week experiment, noted no effects on the growth or reproduction of rats given 7.5 mg of copper as acetate, although when a like amount was given as basic acetate reproduction was affected. A safe daily intake of 5 mg per day for rats when expressed in relation to body weight might range from 12.5 to 25 mg per kilogram. This is considerably greater than the amount Kiyooka[60] regarded as safe for rabbits. Cunningham[28] gave daily to one of two adult cows 500 mg of copper as sulfate (1.5 mg per kilogram) and to the other 1,250 mg (3.3 mg per kilogram). They remained well over a period of nine months and calved normally.

Attention was first called to the occurrence of chronic copper poisoning in domestic animals by Ellenberger and Hofmeister[34] in 1883, and by Baum and Seeliger[7] in 1898. The latter observers believed that cats, sheep, goats, and dogs are susceptible in that order. Bisset[14] described the death of sheep near a nickel smelter, following a period in which they had exhibited depression, dullness, emaciation, and weakness. Schaper and Luetje[100] and Beijers[9] have described the disease characterized by icterus and hemoglobinuria as occurring in sheep grazing in orchards that had been sprayed with Bordeaux mixture. In Texas, large numbers of fatalities occurred among sheep that had had access for 25 to 86 days to a proprietary salt-lick with 5 to 9 per cent of copper sulfate intended for use in eradicating stomach worms. Boughton and Hardy[17] estimated that the fatally poisoned animals had ingested from 40 to 49 grams of copper sulfate.

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Chapter 44

Copper in the Production and Nutritional Quality of Crops

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Copper is one of five or six mineral elements, commonly called micronutrient or minor elements, now generally recognized as essential to the nutrition of plants and animals. Especially with respect to plants, it is considered that other elements cannot be substituted for copper and that it plays an essential and peculiar role in their metabolic processes. Nearly a century before these discoveries were made, copper was recognized as a constituent of plant tissue and there are many references in the literature[6] to the content of copper in plants in relation to soils and geological formations.

In common with the early concepts of boron in relation to crop yields, copper salts were first considered only as toxic substances. Thus Brenchly[13], in 1910, in an intensive study found that a concentration of 0.2 ppm of copper in a nutrient solution retarded the growth of barley plants. Had the techniques and concepts of today been available to her, she no doubt would have discovered the essentiality to plants of much smaller supplies of copper. Soon thereafter Lutman[37] noted that in Vermont potatoes sprayed with Bordeaux mixture yielded much better than did untreated plants, even in the absence of any evidence of blight. Later Floyd[22] reported that "dieback," a physiological disorder of citrus and other trees in Florida, was corrected by Bordeaux spray. It has been reported* that copper sulfate was used as early as 1885 in the Everglades region on citrus and other crops to obtain better growth. It was not until 1931, however, that Sommer[49] and Lipman and MacKinney[33] presented evidence of the essentiality of copper in the nutrition of the plant.

Many plant species appear to have a relatively higher requirement than normal for one or more of the mineral nutrients. Such plants will often exhibit marked symptoms of physiological disturbances where a specific mineral element is deficient in the soil. Others will accumulate in their tissues very large quantities of an element present in excess in the soil even in those situations where the plant has no apparent need for all or even part of that absorbed. A number of plants of economic importance show some of these relationships to copper. Thus, citrus trees, some of the deciduous fruit trees, the tung tree, and the onion develop more or less specific symptoms of copper deficiency, excellent descriptions of which are now available in the literature[5, 14]. These plants due to their high requirements for copper are good indicator plants for detecting soils having low levels of copper supply. Many of the vegetables, cereals, legumes, and root crops, as well as cotton, tobacco, and others, have shown definite yield response to application of copper salts on certain soils. Occasionally, where copper is quite limiting such crops will exhibit, in addition to retarded growth, deficiency symptoms that are less specific than ordinarily observed in the indicator-type plants. Very few plants have been known that can accumulate large amounts of copper without toxic effects becoming apparent. Thus, the range of copper content found in plants is rather narrow. It is seldom less than 3 ppm except in the case of extreme deficiency and is seldom greater than 20 ppm without exhibiting signs of toxicity.

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* Personal communication of O. C. Bryan to W. O. Robinson.

The Soil—A Reservoir of Copper for Plant Nutrition

Assuming an average yield and copper content, a cutting of alfalfa might remove from an acre of surface soil about 0.6 ounce of copper or 1½ ounces of $CuSO_4.5H_2O$, the salt most commonly applied as a soil amendment. Other crops will remove more or less copper depending upon the portion of the plant removed from the soil area as well as the yield and composition. It is apparent, however, that the quantity removed is not great. The total copper content of soil is not known for any extensive areas, but it would appear to be relatively low. Holmes[24] reports values from 9 to 57 ppm copper in the surface horizons of a large number of soils from all parts of the United States, while Wood[51] reports from 60 to 174 ppm in four soils from Oregon. These quantities would be equivalent to about 20 to 350 pounds of copper or 50 to 900 pounds of $CuSO_4.5H_2O$ per acre. Most workers agree that the total copper content bears little relationship to that available to the plant. A very limited number of attempts have been made to measure available quantities of copper in the soil, but none has produced a satisfactory method for the determination of this fraction in terms of different soils and different crop requirements.

The compounds of copper in the soil have been the subject of study, particularly with reference to organic soils, such as peats and mucks. Copper, like the other mineral nutrients in soils, is present in certain mineral forms, most of which are relatively insoluble in dilute acid. The copper in these minerals is slowly released, through weathering and chemical activity, to the soil solution. They may subsequently be adsorbed on the colloidal particles of the soil, be utilized by micro-organisms[25] and become constituents of various organic compounds, or they may be absorbed directly by the plant. The mechanisms by which these or other dispositions occur are not known. Bower and Truog[12] have shown that polyvalent cations, like copper, forming weak bases are adsorbed by soil colloids in much greater quantity per unit than expected from a consideration of monovalent cations. Such cations, furthermore, are displaced with greater difficulty, a possible factor in the availability of an element like copper. Menzel and Jackson[44] reason that the copper ion adsorbed on the soil colloid is probably an hydroxylated monovalent ion. Jamison[28] has reported that absorbed copper in sandy soils in Florida is only slowly replaceable.

The problems of copper fixation and availability to plants in organic soils is of considerable economic importance in various parts of the world. Dawson and Nair[17] investigated the nature of some copper complexes of possible occurrence in peat soils and concluded that some combination of protein and lignin, involving the phenolic OH group of lignin, is responsible for the formation of both copper and copper ammonia complexes by peat soils. The magnitude of these reactions of copper has been studied by Lees[31], who reported that 1,600 microequivalents were retained per gram of humic acid from solutions of copper.

Micro-organisms also appear to play an important role in the fixation of copper in organic complexes. Hoffman[23] found that heating organic soils to high temperatures reduced the incidence of copper deficiency diseases, and Hurwitz[26] has reported that while the soluble constituents of plant residues increased the amount of extractable copper from soils, a part of this copper again reverted to an insoluble form when the soils were incubated.

A few interrelationships of copper with other elements in the soil have been reported. Willis and Piland[50] postulated that copper serves as a catalyst in maintaining manganese in an oxidized form, and hence, where excessive concentrations of soluble iron and manganese are present, copper may be helpful in preventing an imbalance of these elements. Liebig, Vanselow, and Chapman[32] reported that aluminum in culture solutions prevented toxic effects of high copper concentrations. Peech[45] found that the solubility of copper added to a Norfolk fine sand was much less at a pH of 6 as compared with a pH of 3, and Purvis and Davidson[46] have confirmed this in other soils.

The distribution of copper deficiency in soils in relation to crop quality and yields has been investigated by Beeson and co-workers[7, 9, 10]. While the areas involved are not large, copper-deficient soils are of considerable economic importance because they occur in relation to both truck crop and fruit production. In general, the Mississippi Valley has been free of these troubles, while the more critical areas include many of the organic soils in the Northeastern United States, the Atlantic Coastal Plain, and Florida. In the Western region the areas of copper deficiency are scattered and are closely related to special crops.

Copper as a Soil Amendment

Lundstrom and Mehring[36] report an average value of 0.005 per cent copper in mixed fertilizers to which no copper salt has been added. Hence, the quantity added to the soil from as much as a ton of fertilizer would be negligible. The use of copper sulfate, however, has increased steadily since 1890[43], when about 10 tons was used annually. In 1937 consumption had increased to 2,500 short tons. More recent data obtained from A. L. Mehring* of the Bureau of Plant Industry, Soils, and Agricultural Engineering show an estimated consumption in 1950 of 30,000 tons used as a fertilizer. The total agricultural use according to the Bureau of Mines was 50,000 tons in 1944. Of the latter quantity, according to Mehring, 9,516 tons was shipped to Florida and 4,934 tons was sent to California.

Recommendations as to quantities of copper sulfate per acre vary somewhat with the crop, the method of application, and the type of soil. Allison[1] recommends ¼ to 1 pound per tree for citrus, or 50 to 75 pounds of bluestone per acre on muck soils in Florida. Knott[29] recommended up to 300 pounds of copper sulfate per acre for onions on New York mucks. On some mineral soils in Florida, Dickey, Drosdoff, and Hamilton[18] recommend as little as ⅙ ounce of copper sulfate applied as a solution to young tung trees. In general, applications of 20 to 50 pounds of $CuSO_4.5H_2O$ per acre appear to meet most requirements of cultivated crops.

Application of copper compounds to pasture in Australia and New Zealand has proved to be a reliable and economical method of preventing copper deficiency in sheep. Riceman[47] has found that applications of 7 pounds of $CuSO_4.5H_2O$ per acre to a mixed pasture corrected a copper deficiency for several years. Cunningham and Perrin[15] have reported that 5 pounds of this salt had a residual effect in pasture for three years after top-dressing.

Only a limited amount of study has been made of copper carriers. Cunningham and Perrin[15] have warned against the use of insoluble forms of copper compounds for top-dressing of pastures. Stock may ingest abnormally large quantities of copper in a form that adheres to the vegetation. Jamison[30] has studied particle size in relation to the solubility of copper sulfate. Large sizes were leached more rapidly than small sizes, an observation that supported field experience. Armiger *et al.*[2] have reported that copper pyrophosphate, a spent catalyst, was a good source of copper for winter oats and shallu. No toxic effects were noted at the level studied.

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* Personal communication.

Copper in the Plant

The leaves of legumes contain about 50 per cent more copper than do the stems according to a study made by Beeson and MacDonald[11]. Furthermore, the copper content of the above ground portion of the legume plant is higher than that of timothy when grown on the same soil. It appears that the copper content of plants is highest at the earliest stages of growth, and in timothy it can become critically low in the mature plant with respect to animal requirements. In other studies of grasses[8] it was shown that Kentucky bluegrass contained about four times as much copper as timothy when grown under uniform conditions. Bromegrass had twice the copper content found in quack grass. Of 15 grasses studied about half contained more than 10 ppm of copper while four contained less than 7 ppm.

Drosdoff[19] has shown that symptoms of copper deficiency appear in tung leaves when the copper content lies between 3.5 and 4.0 ppm. Bailey and McHargue[4] found as much or more copper in copper-deficient tomato plants as in normal plants. Similar results were obtained in the author's laboratory. Lyon and Beeson[38] found a relatively small increase in the copper content of tomato plants as the copper content of the nutrient solution was increased from 0.02 to 50 ppm. Definite retardation of growth and toxicity symptoms were noted at a level of 12.5 ppm of copper in the nutrient solution.

A comprehensive review of the role of copper in higher plants has been prepared by Erkama[20]. Other pertinent papers may be found in the report of the symposium on copper held at the Johns Hopkins University in 1950[42]. Copper is a constituent of the oxidases of ascorbic acid, *p*-phenylenediamine, and polyphenols, such as tyrosine. Lyon, Beeson, and Ellis[39] reported no effect of a copper-deficient nutrient medium on the ascorbic acid content of tomatoes, although a retarded growth with no difference in the copper content of the leaf resulted. Lyon and Beeson[38] did find, however, that in the presence of an excess of copper, ascorbic acid content in the plant was lower than normal and growth was retarded. It would appear possible that an excess of copper in the plant tissue might be associated with increased activity of an enzyme such as ascorbic acid oxidase with a resultant greater oxidation of ascorbic acid to dehydroascorbic acid. This view appears to find support in the work of Bailey and McHargue[4].

Loustalot *et al.*[34] have reported a significantly reduced rate of photosynthesis in the leaves of young tung trees grown on a copper-deficient medium. According to Arnon[3] there is still only indirect evidence of a function of copper in photosynthesis. Lucas[35] has reported that copper applied to a muck soil in the greenhouse resulted in a significant increase in the ascorbic acid content of spinach in the fall but not in the spring. Investigations of samples grown in the field failed to confirm the greenhouse work. Conflicting results of this kind are typical and indicate important deficiencies in our knowledge of copper metabolism.

The Role of Plants in Supplying the Copper Requirements of Animals

The copper content of plants may vary over a considerable range[6], but an average of 10 ppm for forages would probably be reasonable for practical feeding considerations. Estimations of the quantity of copper required by sheep vary, but Marston, Lee, and McDonald[11] have reported that supplements of 5 to 10 mg of copper per day will provide sufficient protection in most instances. Assuming that a 100-pound lamb eats 2.5 pounds of dry matter daily, a pasture containing 5 to 10 ppm of copper (dry-matter basis) would supply approximately 5.6 to 11.3 mg of copper daily. Since deficiencies are often associated with pastures containing 2 to 4 ppm of copper, it is clear that 7 to 10 ppm in the plant may be the minimum, assuming 100 per cent availability for optimum growth and reproduction. Extensive areas in the United States do not produce forages meeting this minimum requirement. In some, only cattle are involved, and the requirement per unit of weight of feed may be lower than for sheep.

The considerations noted above are based on the assumption that a simple copper deficiency exists. This is not the case in some areas, notably England[21] and Florida[16], where an excess of molybdenum in the forage results in a toxicity in cattle that can be prevented by copper therapy. Troubles on organic soils where both copper and molybdenum are low in the vegetation are well known[27].

The problem of copper deficiency in animals has been adequately treated by Russell[48] and is the subject of another chapter in this monograph (see p. 855). Sheep and cattle dependent upon grazing are particularly susceptible, and are the best indicators of a copper-deficient soil. According to Marston and Lee[40], not only growth and health, but also the rate of wool production and its quality are affected in sheep suffering from a lack of copper. The quality problem, they believe, is specifically related to the deficiency. Other than in the most acutely deficient areas, described by these authors, or those areas where molybdenum toxicity is a problem, there is little or no knowledge of the economic losses from animals that might be traced to a low copper level in soils and herbage.

It is apparent that research workers are on only the threshhold of understanding the biological roles of copper. Only a minimum of knowledge necessary for the most superficial corrective measures is available where soil deficiencies occur. The problems concerning copper are intricate, but their eventual solution will contribute much to a better understanding of the chemistry of the soil and nutrition of plants, animals, and man.

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Chapter 45

Metallography of Copper and Its Alloys

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Metallurgy as a science can be roughly dated from the first application of the microscope to the study of the internal structure of metals. Initially, limited information was obtained by such examination of fractured surfaces, but progress became rapid after Sorby in 1864 demonstrated that a polished and etched section through a metal could reveal many more details of internal structure. Microscopy is still the basic tool of the metallurgist and, while other techniques, such as the use of x-rays and electron beams, have added greatly to the means at his disposal for revealing internal structures, it has, itself, been subject to refinements in methods for producing highly polished surfaces, to the development of improved chemical etchants, and to improvements in microscope design.

Interest in the internal structure of a metal need not be confined to those details which can be seen only after magnification. Indeed, the techniques of micrography, polishing and etching, were first employed by Widmanstätten in 1820 to demonstrate the macroscopic structure of meteorites. The modern metallographer uses these techniques both for the macroscopic and microscopic examination of metals and recent usage has tended to limit the term "metallography" to this particular aspect of the study of metals. The distinction between "macroscopic" and "microscopic" examination is not sharp and might roughly be placed at magnifications of 5 or 10 diameters. The former, of course, includes any structures which can be observed with the unaided eye.

Selection of Representative Sections

As the metallographer approaches a given problem, he is at first faced with the selection of the appropriate section to be examined. Ordinarily this is readily dictated by the problem. For instance, the size and shape of the grains in a casting will be shown most completely by a longitudinal section through the whole casting at an angle determined by its external dimensions. Or, the distribution of a second phase in a rod or wire will be revealed best by a transverse section since the fabrication process causes it to be strung out parallel to the axis of the rod or wire and a random transverse section is likely to intersect it. Longitudinal sections can indicate roughly the amount of deformation by the elongated shape of the grain. The sectioning is generally accomplished with a saw. Large units for macroscopic examination can be given a plane surface with a shaper or coarse file. A file or belt sander is satisfactory for accomplishing this on smaller specimens.

Polishing

Further preparation of the surface may not be required for macroscopic examination, particularly if the grain structure is the subject. This grain structure is revealed by deep etching. Nitric acid, 20 to 50 per cent of concentrated HNO_3 by volume, serves well for macroscopic examination of copper and most of its alloys. Discontinuities, such as pinholes, shrinkage, fissures, etc., are most easily observed in the unetched surface. In such cases, rubbing the specimen on fine abrasive papers, supported on a smooth hard surface, down to 00 or 000 emery may be necessary to remove metal which has flowed over fine discontinuities during the preliminary smoothing operations.

Surface preparation for microscopic examination involves the use of specimens which are small enough to be held against a moving abrasive surface. For copper and its alloys, polished on rotating cloth surfaces which are wet with suspensions of abrasives, rotational speeds of about 1,750 rpm can be used without having abrasive particles become embedded in the surface of the metal. The difficulty of holding small or irregularly shaped specimens against the cloth is avoided by mounting them in thermoplastic or thermosetting plastics under pressure. Adequate preparation of a specimen which is to be etched involves three grades of abrasive, (1) 220 emery, (2) tripoli or 600X alundum, and (3) levigated alumina. Rounding of edges cannot be avoided when cloth-covered wheels are employed. Whenever structures at such edges must be examined, a sharp edge can be obtained by polishing on slowly rotating paraffin wheels for the last two abrasives.

Electrolytic Polishing

Originating in the early work of P. Jacquet, surface preparation by electropolishing has become rather common. Briefly, the process involves using the specimen as anode in an appropriate electrolyte, while maintaining the voltage and current density at a level determined by the metal and the electrolyte. Most copper alloys can be electropolished in rather concentrated phosphoric acid. Rapid polishing at high voltages and current densities will give a polished and etched surface for routine grain-size determinations. Much better surfaces can be obtained at a voltage of about 1.5 volts; the required voltage can usually be determined by gradually increasing the voltage, accompanied by an increase of current, until a sudden increase in voltage is accompanied by a drop in current. If further increase in voltage is restrained with a variable external resistance, a very highly polished surface will be developed on a specimen which has already been mechanically polished in about 3 minutes. It appears that a thin but weakly conducting layer of electrolyte, concentrated with the dissolving metal, retards the dissolution at all parts of the surface except projecting ones. The resulting surface is free of any trace of distortion from the mechanical polishing. It can be etched by lowering the voltage or by using the standard etchants. There is a tendency for exaggeration of voids and holes left by more rapid dissolution of inclusions. Some two-phase alloys can be prepared satisfactorily, while others develop surfaces which are too uneven because of the different potentials of the two phases.

Etching

The polished surface is swabbed with or agitated in an etchant which removes a very thin layer of smeared metal, and the process is continued until the desired amount of grain contrast is achieved. Various etchants, as listed in Tables 45-1 and 45-2, are used for different alloys and for various purposes. The amount of grain contrast depends on a tendency for more rapid chemical attack in some crystallographic directions than in others, so that adjacent grains of different orientation reflect the incident light in different directions. Development of submicroscopic etch pits, also differing with orientation, apparently are also the cause of variations in coloring. The etched specimen is rinsed with water, then alcohol, and then dried.

Microscopy

The prepared specimen is examined with the aid of reflected light on metallurgical microscopes, of which several models are available. For macroscopic work small hand glasses up to 14X are always kept at hand and photographic reproduction is done on low-power microscopes with oblique or normal illumination. For microscopic examination magnifications from about 20X to 4,000X are usually available, the resolution decreasing at the high magnifications. Illumination may be normal to the surface, dark field, or by means of polarized light. Recent techniques include phase-contrast which, as the name implies, results in differences in brightness according to differences in phase of the light reflected from surfaces at different levels.

TABLE 45-1. ETCHANTS USED IN ROUTINE EXAMINATION OF COPPER AND COPPER ALLOYS*

No.	Etchant	Remarks
1	NH_4OH .... 5 parts H_2O_2 (3%) .... 2 to 5 parts with or without 5 parts H_2O	Fresh solution made up just before use.
2	NH_4OH .... 10 ml H_2O_2 (3%) .... 4 ml KOH (20%) .... 1 ml H_2O .... 5 ml	KOH prevents oxide film. Fresh solution made up just before use.
3	*Electrolytic* $FeSO_4$ .... 30 g NaOH .... 4 g H_2SO_4 (conc.) .... 100 ml H_2O .... 1900 ml	Can also be used following 1 or 5 for coloring copper and high-copper alloys. Circuit includes dry cell, a platinum wire cathode and the specimen as anode. The polished surface is dipped just under the surface.
4	CrO_3 .... 40 g NH_4Cl .... 7.5 g HNO_3 (conc.) .... 50 ml H_2SO_4 (conc.) .... 50 ml H_2O to make 1 liter........ 1900 ml	Also used for macrostructure. The degree of contrast can be modified by adding a few drops of HNO_3 or H_2SO_4 to the etching bath as desired.
5	$K_2Cr_2O_7$ .... 2 g NaCl .... 1.5 g H_2SO_4 (conc.) .... 8 ml H_2O .... 100 ml	Also used for macrostructure.
6	HNO_3 (conc.) .... 75 ml Glacial acetic acid .... 25 ml	Also used for macrostructure. Fresh solution is made up just before use. Specimen should be dry.
7	(a) (b) $FeCl_3$ .... 5 g 10 g HCl .... 10 ml 25 ml H_2O .... 100 ml 100 ml	Also used for macrostructure.
8	HNO_3 .... various conc.	For macrostructure. Trace of $AgNO_3$ gives brilliance.
9	$(NH_4)_2S_2O_8$, 10% solution	Follows 8, for improving contrast.

* From "The Metals Handbook," American Society for Metals, Cleveland, Ohio, 1948.

The Purposes and Scope of Metallography as Applied to Copper and its Alloys

Interest in the internal structures of copper and its alloys as revealed by metallography applies to a field far too extensive to be covered in this chapter. It is rather the purpose of this section to give illustrations of how metallography is applied in a number of cases, from which its application to other structures may readily be deduced. The structures which the metallographer investigates may conveniently be divided into two groups: those which arise on solidification—cast structures, and those which result from deformation and annealing—wrought structures. His

TABLE 45-2. ETCHANTS USED FOR VARIOUS COPPER ALLOYS*

Alloy[a]	Etchant[b]	Remarks
Copper and dilute copper alloys	4 or 5	....
Brass, alpha, 85 to 100%	4, 5 or 1 then 7	7 follows 1 to develop contrast
Brass, alpha, 65 to 85%	1	....
Brass, alpha-beta	1 or 1 then 7	7 follows 1 to darken beta
Phosphor (tin) bronze	4, 5 or 1	....
Tin brass	1	....
Silicon brass	4 or 1	....
Silicon bronze	4 or 5	....
Aluminum bronze, alpha	5 or 4	....
Aluminum bronze, alpha-beta	1 or 1 then 7	7 follows 1 to darken beta
Aluminum-silicon bronze	2 or 5	....
Manganese bronze	1 or 1 then 7	7 follows 1 to darken beta
Nickel silver	4, 5 or 6	....
Cupro-nickel	3, 4 or 5	3 minimizes appearance of coring
Beryllium bronze	5 or 1	1 used for detecting small quantities of beta

[a] For leaded alloys, use the etchant recommended for matrix.

[b] Numbers, given in order of preference, refer to the etchants listed in Table 45-1.

Note. These etchants are commonly used for ordinary examination. When other etchants are sought for special purposes, reference can be made to ASTM Tentative Method E 3-46T.

* From "The Metals Handbook," American Society for Metals, Cleveland, Ohio, 1948.

purpose is to observe the structure of castings and to follow the changes in structure which result from fabrication in order that he may assist in avoiding failures during fabrication, in insuring good quality and correct properties in the finished product, and in developing new processes and alloys.

Cast structures are examined *macroscopically* to determine among other things whether the sizes and shapes of the cast grains are such that trouble might be expected in fabrication, whether the contracting solid metal has left unfilled cavities, and whether the release of gases has formed voids. The series of ingots, shown as deeply etched longitudinal sections in Figure 45-1, illustrates structural changes resulting from different treatments of the molten metal. Variations in grain shape are apparent; moreover, the top shrinkage and the central voids tell a story about the release of gases. One of the foundryman's major problems is the proper feeding of intricate cast shapes with molten metal. Failure to fill shrinkage cavities may be revealed by nondestructive radiographic testing, but lacking these facilities it can be shown by sectioning representative samples. The shrinkage cavities in a small silicon bronze casting are revealed metallographically in Figure 45-2 by light use of an etchant which minimizes grain contrast.

Microscopic examination of cast structures is used to show nonuni-

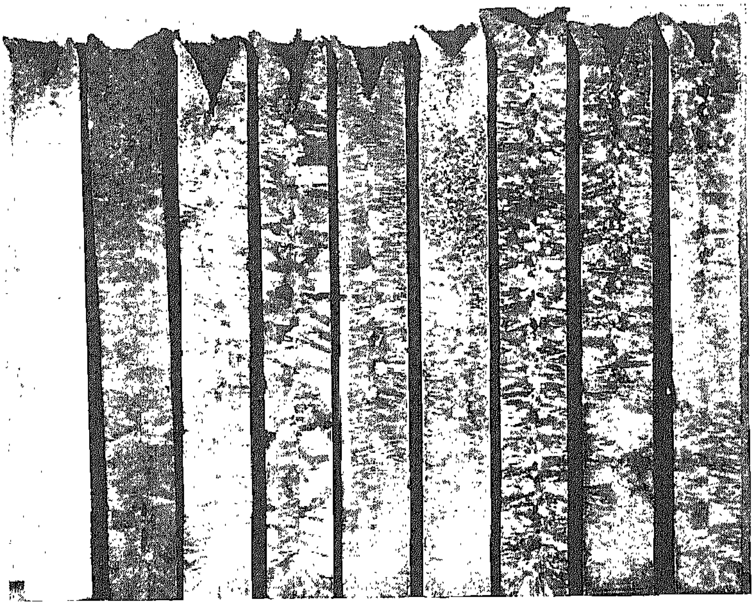

FIGURE 45-1. Small castings of silicon bronze which show the effect of small additions of several different impurities on the cast macrostructure. ⅔X, reduced 20 per cent. (*Courtesy of the Central Laboratory of The American Brass Company.*)

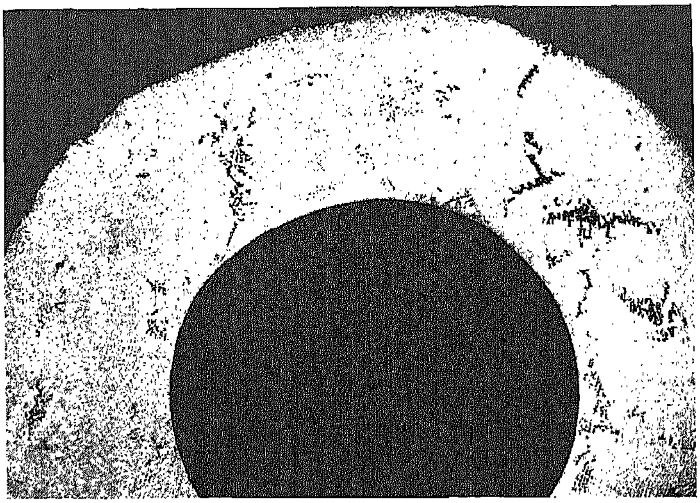

FIGURE 45-2. The macrostructure of a small silicon bronze casting, showing dendrites and shrinkage cavities. Magnification 3⅓X. (*Courtesy of the Central Laboratory of The American Brass Company.*)

formity of composition in alloys. Normal cooling of alloy castings leaves structures which are far from being in equilibrium, the first dendritic nuclei of solidification differing in composition from the last parts to solidify. Generally this is readily demonstrated by the differences in rate of attack of the etchants, and whenever it is desired to render the structure homogeneous by heat treatment, the progress of the treatment can be followed metallographically. Microscopic examination is used to show the presence of separate phases. Nonequilibrium departure from compositional uniformity frequently is great enough to cause a second phase to appear in an alloy which in equilibrium would be a single-phase alloy, as seen in the cast microstructure of the phosphor bronze with 10 per cent tin shown in Figure 45-3. Of course, the amount of second phase in a two-phase alloy is also a matter of interest. A nonmetallic second phase may appear in a casting, such as the cuprous oxide shown in a eutectic with copper in Figure 28-1, page 616. This is the normal structure of cast tough-pitch copper. This oxide is usually identified positively when polarized light reflected from the back of the particle reveals its ruby color. Fine fissures which can only be revealed by microscopic techniques may also sometimes occur in castings.

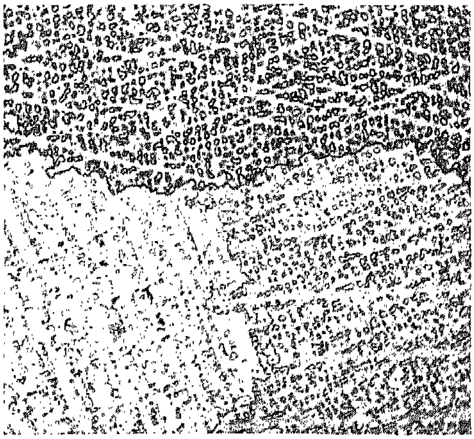

FIGURE 45-3. The cast microstructure of a 10 per cent tin bronze. Magnification 75X. (*Courtesy of the Central Laboratory of The American Brass Company.*)

Some features of wrought metal are of large enough magnitude to lend themselves to macroscopic examination. In this case the surface preparation, however, usually needs to be more careful than for cast structures. The nonuniform grain structure of cartridge cases is examined on a longitudinal section through the whole case. Sections through partially

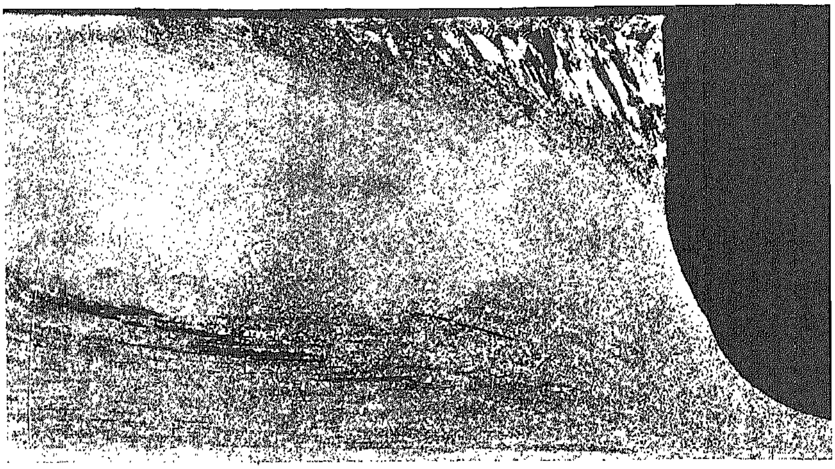

Figure 45-4. Longitudinal section through one half of a partially extruded tube billet of cartridge brass. Etched with $NH_4OH + H_2O_2$. Approximately actual size. (*Courtesy of the Central Laboratory of The American Brass Company.*)

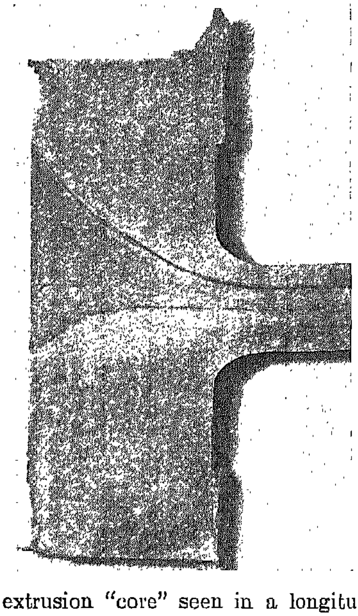

Figure 45-5. Origin of extrusion "core" seen in a longitudinal section through the butt of an extruded leaded brass rod. ½X. (*Courtesy of the Central Laboratory of The American Brass Company.*)

pierced or extruded billets are very informative with respect to these manufacturing processes. As a part of a study of billet lubrication, the partially extruded brass tube billet shown in Figure 45-4 was photographed to show the flow of metal by means of the accompanying grain refinement. In this case an etchant giving maximum grain contrast was desired. In contrast to this, a partially extruded billet for a leaded brass rod was etched lightly (Figure 45-5) to show the origin of a rod defect. This defect, called "core," results from flow of the oxidized back of the billet into the center. Grain contrast would have hidden the contrast between metal and oxide.

One of the commonest applications of microscopic examination to wrought copper and copper alloys is the determination of the state of the metal with regard to cold working and annealing. Heavily drawn wire, in longitudinal section, has the appearance shown in Figure 45-6. (This illustration also serves as an example of the important use of metallography for the examination and detection of defects.) Lighter working results in lesser elongation of the grains, and the large grains in Figure 45-7 are indicative of about 50 per cent reduction of cross-sectional area. This structure as a whole indicates that a low-temperature anneal has resulted in only partial recrystallization. Further annealing completes the recrystallization and the new grains grow to sizes determined by the metal or alloy, its purity, its prior history, and in particular the time and temperature of annealing. The properties of annealed metal vary with the grain size, and the requirements of specifications for mill products make the determination of grain size perhaps the most common application of metallography.

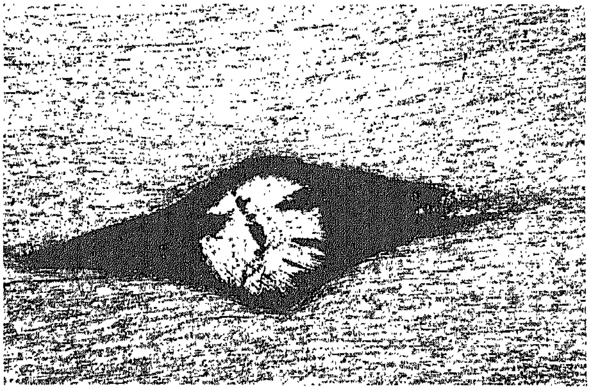

FIGURE 45-6. Detail of a large inclusion in heavily drawn commercial bronze wire (90 Cu-10 Zn) as seen in a longitudinal section. Magnification 75X. (*Courtesy of the Central Laboratory of The American Brass Company.*)

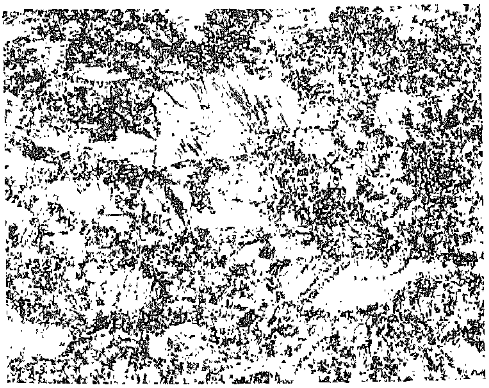

Figure 45-7. Microstructure of a manganese-bearing brass annealed ½ hour after being rolled to 50 per cent reduction. Magnification 75X. (*Courtesy of the Central Laboratory of The American Brass Company.*)

The reasons for metal failures in service can frequently be determined with the aid of metallography. If the neighborhood of the breakdown shows a decrease in thickness and a grain elongation, it can be concluded that it has been stressed beyond its tensile strength. On the other hand, a fatigue failure, which shows no distortion in the neighboring metal, is suspected when it can be determined that the crack passes straight through the grains, and positively identified when the adjacent undistorted grains are the only ones which show deformation markings. Corrosion failures are readily identified, but the metallographer is frequently called upon to use his photographic experience to record the nature of corrosive attack. For example, Figure 45-8 shows an elongated pit on the

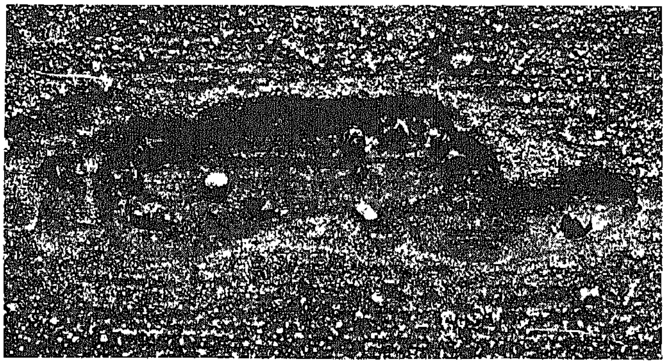

Figure 45-8. Crystals of copper from dezincification in a pit on the inner surface of an admiralty condenser tube. Magnification 10X. (*Courtesy of the Central Laboratory of The American Brass Company.*)

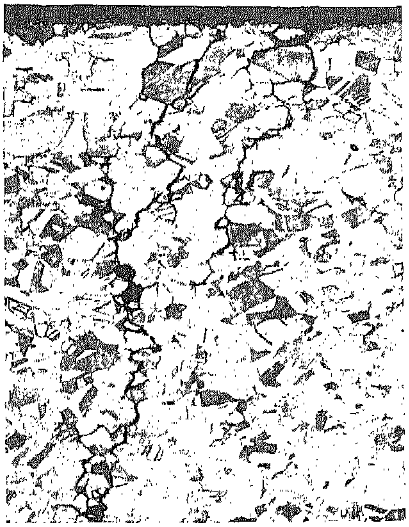

FIGURE 45-9. Stress-corrosion cracking in 70-30 brass. Magnification 75X. (*Courtesy of the Central Laboratory of The American Brass Company.*)

inside of an admiralty condenser tube. This example shows the very unusual feature of small copper crystals, the product of dezincification (*cf.* Chapter 18), projecting from the bottom of the pit. The particular type of stress-corrosion cracking characteristically found in brass, which

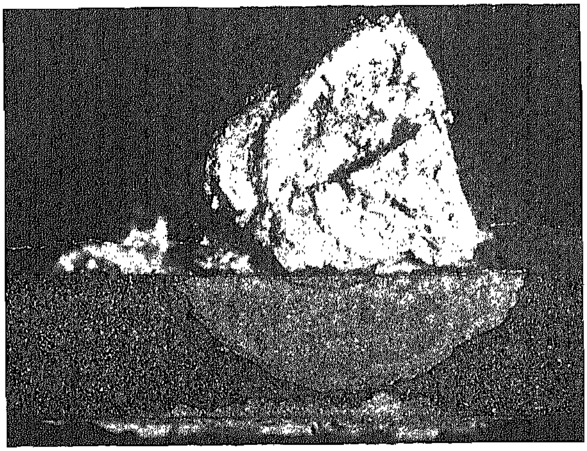

FIGURE 45-10. Plug-type dezincification in leaded brass pipe with nodule of corrosion products attached. Magnification 6X. (*Courtesy of the Central Laboratory of The American Brass Company.*)

is known as season cracking (*cf.* Chapter 18), is often recognized by an intergranular cracking such as is illustrated in Figure 45-9. However, failures of copper and its alloys from stress-corrosion have been known which are transgranular in nature. At times, the loosely adhering fragile hump of corrosion products in contact with a dezincification plug is still present when the metallographer receives the sample. The photographic reproduction of a section through such a hump and the adjacent metal, as shown in Figure 45-10, is unusual and this photograph was awarded a first prize in a National Metals Congress competition.

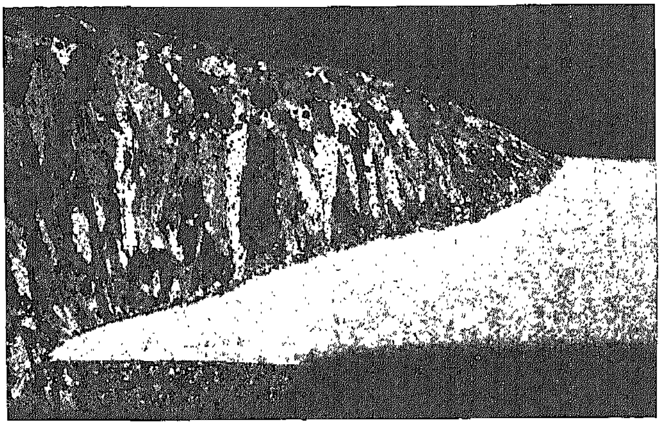

FIGURE 45-11. Section through experimental butt weld showing gas porosity, cast structure of filler metal (left), and grain growth in base metal (right). Magnification 6X. (*Courtesy of the Central Laboratory of The American Brass Company.*)

Welds might be considered as hybrids of the cast and wrought structures when wrought metals are joined. They are examined metallographically for gas porosity, cohesion, compositional uniformity, etc., in the cast structure and for any effect on the wrought structure resulting from the high temperature. The example of a weld which shows several of these defects, shown in Figure 45-11, was obtained in the course of an experimental investigation of methods for butt welding red brass with a phosphor-bronze filler.

References

1. Kehl, G. L., "Principles of Metallographic Laboratory Practice," New York, McGraw-Hill Book Company, Inc., 1943.
2. "The Metals Handbook," American Society for Metals, Cleveland, Ohio, 1948.
3. "A.S.T.M. Standards," American Society for Testing Materials, Philadelphia, 1952:
    E2—44T, "Preparation of Micrographs of Metals and Alloys."
    E3—46T, "Preparation of Metallographic Specimens."

Chapter 46

The Analytical Chemistry of Copper

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In this chapter the analytical chemistry of copper is reviewed rather briefly. Due to space limitations no attempt is made to give the details of the laboratory procedures, which may be found by consulting the references cited. Recent literature is emphasized since the older work is reviewed and summarized elsewhere; for example, Rüdisüle[83] covers the literature through 1932 and gives procedures and references. Special techniques, such as spectrographic, polarographic, amperometric titrations, microvolumetric, and microgravimetric, have not been included.

DETECTION

Copper is a member of the hydrogen sulfide group (Group II) in the usual qualitative scheme[68] and is separated from later groups by precipitation as black cupric sulfide from a $0.25N$ hydrochloric acid solution. The sulfide is soluble in hot dilute nitric acid but insoluble in ammonium polysulfide solution, which separates it from arsenic, antimony, tin, molybdenum, etc.

Other characteristic qualitative reactions of the cupric ion are as follows:

(a) Formation of deep blue cupric ammonia complex ion upon the addition of excess ammonium hydroxide solution.

(b) Precipitation of brown cupric ferrocyanide from acetic acid solution.

(c) Addition of potassium iodide to give free iodine and a precipitate of cuprous iodide.

Feigl[37] makes considerable use of the following spot tests, which have been recommended recently[96] for more general qualitative use because of their sensitivity and selectivity:

(a) The addition of zinc sulfate and ammonium mercurithiocyanate to give a precipitate of zinc mercurithiocyanate colored purple by the corresponding cupric salt.

(b) The catalytic acceleration of the reduction (decolorization) of ferric thiocyanate complex by alkaline thiosulfate solution.

(c) Formation of a green cupric complex with dithio-oxamide (rubeanic acid).

(d) Reaction with alizarin blue, which, according to Feigl and Caldos[37a], is the most sensitive of all tests for copper.

Welcher[95] gives an extensive list of organic reagents which may be used for the detection of copper.

SEPARATION

The most useful reactions for the separation of copper are those involving the precipitation of cupric sulfide, cuprous thiocyanate, cupric hydroxide, and metallic copper.

Copper may be separated from elements other than those of the hydrogen sulfide qualitative group by precipitation with hydrogen sulfide from 0.25N hydrochloric or sulfuric acid solution or by the use of sodium thiosulfate[4]. However, some of the interferences, such as arsenic, antimony, tin, molybdenum, bismuth, lead, and silver, are of common occurrence. By precipitation with sodium sulfide from sodium hydroxide solution[48] a separation from arsenic, antimony, tin, and molybdenum can be effected.

The precipitation of cuprous thiocyanate affords a useful separation of copper from most elements except silver, lead, mercury, selenium, tellurium, gold, and the platinum metals. It may be carried out from a slightly acid sulfate or chloride solution, but nitrate must be absent. The copper is reduced to the cuprous state most conveniently by a sulfite and the addition of a soluble thiocyanate causes the precipitation of white cuprous thiocyanate[54]. A tartrate may be added to prevent the precipitation of easily hydrolyzed metal ions.

The precipitation of cupric hydroxide by sodium hydroxide serves to separate copper from molybdenum, tungsten, vanadium, and arsenic, provided that the final solution contains an excess of not more than 5 grams of sodium hydroxide in 100 ml.

Elemental copper can be precipitated on a more electropositive metal such as aluminum. Small strips or squares of aluminum foil with turned-up corners are most convenient. The solution should contain 10 per cent of concentrated sulfuric acid. If chloride or nitrate is present, it must be removed by fuming after the addition of the sulfuric acid. Boiling for 10 minutes in the presence of the aluminum foil usually brings about the complete reduction of the copper. Any small amount of copper remaining in solution may be separated with hydrogen sulfide. The copper may be dissolved in nitric acid and any of the usual methods of determination applied. The main use of this method is to separate copper from iron. It is not a separation from gold, silver, platinum, mercury, tin, bismuth, cadmium, selenium, tellurium, cobalt, nickel, or thallium[62].

METHODS OF DETERMINATION

Electrodeposition of Metallic Copper

It is possible to deposit copper quantitatively in a dense, adherent, pure form at the cathode provided that certain interfering substances are absent and that the conditions are properly controlled.

The electrolytic method is generally considered to be one of the most accurate methods for the determination of copper. It is the only method whereby 5 or 10 grams of copper may be handled and therefore is the standard procedure for the analysis of electrolytic copper and other materials with very high copper contents.

A number of conditions affect the character and purity of the deposit and the rate of deposition. Since a change in one condition may necessitate changes in other conditions, a large number of possible combinations exist[16].

The various methods may be classified as "slow" or "rapid" according to the rate of deposition. The slow methods are used when the highest accuracy is desired, such as in the analysis of electrolytic copper, Lake copper, etc. At a current density of 0.6 amp per sq dm (5.6 amp per sq ft) 5 grams of copper can be deposited in 16 hours on a cathode cylinder of the size commonly used (about 0.4 dm in area).

The rapid methods involve the use of efficient stirring devices to bring the copper ions to the cathode, making it possible to apply a high current density. Circulation may be effected by rotating the anode or cathode, by a current of air, or by means of an electromagnetic field[80]. Using a gauze cathode, 5 grams of copper may be deposited in 4 hours at a current density of 4 amp per sq dm (37 amp per sq ft).

The deposition is usually made from an acid solution. The most commonly used electrolyte contains both sulfuric and nitric acids (2 ml conc. sulfuric acid and 1 ml conc. nitric acid in 100 ml of solution). Nitric acid alone is not satisfactory, but the addition of one or two drops of 0.1*N* hydrochloric acid solution brings about a rapid, smooth deposition[85]. The amount of hydrochloric acid must be limited to the stated amount since larger quantities may cause the dissolving of platinum from the anode and its subsequent deposition at the cathode.

The substances which interfere with the electrolytic method are gold, silver, platinum metals, mercury, selenium, tellurium, arsenic, antimony, bismuth, tin, molybdenum, iron, chloride, nitrous acid, and organic matter.

Gold, platinum metals, mercury, and silver deposit at considerably lower cathode potentials than copper and therefore will be completely deposited with the copper. These elements may be determined by other means and corrections applied to the weight of the deposit. However, the character of such a deposit may be poor. For example, the presence of more than 0.2 per cent silver causes a loose crystalline deposit which is not suitable for weighing. In this case the quality of the deposit may be improved by applying a very low current density (0.01 to 0.03 amp) until the silver has deposited and then increasing it for the deposition of the copper. It is also common practice to precipitate the silver as silver chloride before the electrolysis[86].

Bismuth may be removed most conveniently as the basic nitrate or carbonate[48].

The most certain means of eliminating interference from selenium and tellurium is to remove them as the elements by reduction with sulfur dioxide[6].

Selenium and tellurium in the form of selenate and tellurate cause no interference. Selenium may be oxidized to selenate by boiling the ammoniacal solution with 1 or 2 grams of potassium peroxydisulfate. The addition of 0.02 to 0.04 gram of manganese as manganous nitrate is said to prevent interference from tellurium through oxidation by the permanganate formed during electrolysis[80]. Recently the direct addition of potassium permanganate to form selenate and tellurate has been recommended[75].

Limited amounts of arsenic can be held in solution by the addition of ammonium nitrate or by increasing the concentration of nitric acid[6]. The addition of hydrogen peroxide before and during the electrolysis is helpful in the presence of small amounts of arsenic and antimony[5] and in the presence of considerable quantities of arsenic if antimony is absent[10].

Copper may be separated from arsenic and antimony by deposition from an ammoniacal fluoride solution[13] or from a nitric-hydrofluoric acid solution[8]. Newton and Furman[73] have shown that it is possible to determine copper in the presence of arsenic, antimony, selenium, and tellurium by two electrolyses after peroxydisulfate oxidation, the first in fluoride solution and the second in acid or ammoniacal solution.

The presence of nitrous acid (nitric oxide or nitrogen dioxide) may prevent the complete deposition of copper or even cause the deposit to redissolve. It may be removed by boiling or by the addition of urea or sulfamic acid[87].

Small amounts of ferric iron (0.5 per cent) cause no trouble, but larger amounts may prevent the complete deposition of copper. By keeping the nitrate and nitric acid concentrations low, the error may be minimized. The addition of phosphate[42] or fluoride[38] will eliminate the interference from even large amounts of iron and may be used in the determination of copper in iron and steel as well as in brasses, bronzes, aluminum alloys, etc.[56, 74, 82].

Organic matter may be removed by dry ashing or one of the usual wet treatments such as digestion with sulfuric and nitric acids or sulfuric, nitric, and perchloric acids[91].

A discolored copper deposit indicates the presence of impurities. Such a deposit may be purified by dissolving and redepositing it. In the presence of considerable impurity it is preferable to add a small amount of a ferric salt and then ammonium hydroxide in slight excess. Impurities such as antimony, arsenic, and bismuth are precipitated along with the hydrous ferric oxide[6]. Since the ferric oxide coprecipitates a small amount of copper, a reprecipitation must be made.

For brass and related alloys, the above procedures may be modified to include the simultaneous or successive electrodeposition of lead dioxide at the anode and copper at the cathode provided that not more than 0.1 gram of lead is present; larger amounts form loose deposits. Tin is removed as metastannic acid after treating the sample with nitric acid. The metastannic acid coprecipitates a small amount of copper which must be recovered[5, 19, 26]. The usual electrolyte is a nitric acid solution containing one drop of $0.1N$ hydrochloric acid[5]. An alternate procedure is to deposit the lead dioxide from a nitric acid solution and then add sulfuric acid to complete the deposition of the copper[9].

Copper can be separated from tin by electrodeposition of the copper from a hydrochloric solution containing hydroxylamine hydrochloride at a limited cathode potential[33]. Electrolysis of a strong sulfuric acid solution or a combination hydrofluoric, nitric, phosphoric acid, hydrogen peroxide solution have also been suggested[75] for separations from tin.

The deposition of copper from an acidic tartrate solution makes possible a separation from large amounts of tin and antimony and has been applied to tin-base as well as copper-base alloys[57].

In the determination of copper in steel, the copper may be separated from iron as cupric sulfide, which is then dissolved in nitric acid and the copper deposited electrolytically. The main interference is molybdenum, which may be separated from copper by treatment of the solution with sodium hydroxide[4].

Considerable attention has been paid recently to the determination of copper in aluminum alloys[1, 2, 76, 90, 94].

By electrolysis at a controlled cathode potential with a mercury cathode and a silver-silver chloride anode, Lingane[58] has devised a coulometric method in which the quantity of current used to deposit the copper is measured with a hydrogen-oxygen coulometer. The determination of copper in the presence of bismuth appears possible.

The electrodeposition of copper may be carried out on a micro scale. The original procedure and apparatus designed by Pregl[81] has been modified[21, 61]. The apparatus of Clarke and Hermance[21] is very convenient and is in wide use. Instead of weighing the copper, it may be dissolved in ceric sulfate solution which is 0.5*M* in hydrochloric acid and the excess back-titrated with ferrous sulfate[18]. The microgravimetric method has been applied to the determination of copper in cast iron[67].

Small amounts of copper may be deposited by internal electrolysis[22] using a platinum cathode and an anode of aluminum, zinc, iron, cadmium, or lead. Liquid amalgams may also be used as anodes[72, 77, 101, 102]. This method is particularly suitable for the separation of small amounts of copper from large quantities of base metals. It has been applied to the determination of copper in lead metal and alloys[23, 24, 65], zinc and its alloys[22, 65, 66], aluminum and magnesium alloys[17], iron[39], nickel[66], cadmium[24, 38], ferrotitanium[14], and iron pyrites[31].

The American Society for Testing Materials recommends internal electrolysis as a means of separating copper, bismuth, and silver from pig lead[7].

Gravimetric Methods

After separating cuprous thiocyanate, it may be dried and weighed or preferably ignited and weighed as cupric oxide. It is likewise possible to ignite cupric sulfide to the oxide, CuO, for weighing[18].

A number of organic reagents precipitate copper as stable compounds of definite composition which may be dried and weighed. The most useful of these reagents are briefly discussed below. Flagg[40] gives an excellent treatment of the use of these reagents, including laboratory procedures and references to the original literature.

Alpha-benzoin oxime added to an ammoniacal or ammoniacal tartrate solution of copper (II) precipitates green flocculent copper alpha-benzoin oxime. The reaction serves to separate copper from such elements as iron, aluminum, nickel, cobalt, zinc, cadmium, lead, and molybdenum.

Salicylaldoxime permits the complete precipitation of copper at a pH of 2.6 to 3.0 where little interference from other metal ions is encountered, although ferric ion is coprecipitated if more than a few milligrams of iron is present.

The reagent 8-hydroxyquinoline (oxine, 8-quinolinol) precipitates copper quantitatively from moderately acid solution as well as from ammoniacal tartrate solution. When it is formed from ammoniacal tartrate solution, separation is made from aluminum, iron, chromium, lead, arsenic, antimony, tin, and bismuth.

Other organic precipitants for copper which may prove useful at times are quinaldic acid, anthranilic acid, benzotriazole, thionalide, cupferron, neocupferron, alpha-nitroso-beta-naphthol, and salicylimine[34].

Volumetric Methods

Iodometric. The iodometric method is the most popular of the volumetric methods and is particularly useful for copper ores. It depends upon the reaction of a cupric salt with potassium iodide in acid solution to form insoluble cuprous iodide and free iodine, the liberated iodine then being titrated with standard sodium thiosulfate solution in the presence of starch indicator.

$$2Cu(C_2H_3O_2)_2 + 4KI \rightarrow 2CuI\downarrow + I_2 + 4KC_2H_3O_2$$

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

It is of wider application than the electrolytic method since there are fewer interferences. The most common interfering substances are iron, arsenic, antimony, molybdenum, and nitrous acid (nitric oxide and nitrogen dioxide). Arsenic, antimony, and iron in moderate amounts can be rendered harmless by the proper control of conditions.

The adjustment of acidity is of great importance, particularly in the presence of arsenic, antimony, and iron. At high acidities, these substances in their higher oxidation states will liberate iodine from iodide ion. Above a pH of 4, however, the reaction between cupric and iodide ions is slow and incomplete.

It is important that any iron, arsenic, and antimony be oxidized completely to their higher oxidation states as well as the copper. This is accomplished by dissolving the sample in nitric acid or nitric and hydrochloric acids, although Crowell[28] points out that some sulfide ores containing iron and arsenic require either a double treatment with nitric and hydrochloric acids or a single treatment followed by bromine water.

The nitric acid solution is usually evaporated to a small volume, neutralized with ammonium hydroxide, and then made acid with acetic acid. The presence of much ammonium acetate[78] or other salts with complex-forming anions[27] retards the liberation of iodine. In the absence of iron, a formate solution has been recommended[27] as being superior to an acetate solution. Hammock and Swift[47] have shown that it is also possible to use a buffered sulfate-hydrogen sulfate solution with a pH of 0.5 to 3.0 in the absence of iron. Pentavalent arsenic and antimony are without effect at a pH of 2.4.

Park[78] has given a procedure for eliminating the interference from ferric iron by complexing it with ammonium bifluoride. Upon buffering the solution to a pH of 3.0 to 3.5 with potassium hydrogen phthalate, good results were obtained in the presence of 0.3 gram of ferric ion and 0.1 gram of arsenic as arsenate. Crowell[29] showed that the phthalate was not necessary since the ammonium bifluoride buffers the solution properly. At a pH of 3.3 as much as 0.3 gram of iron or 0.2 gram of arsenic may be tolerated without effect. More than 20 mg of antimony interfere, probably due to coprecipitation of copper by the precipitated antimonic acid[30]. In the presence of larger amounts of iron, as in cast iron and steel, it is recommended that a preliminary separation of the copper be made with aluminum[63], hydrogen sulfide[64], or sodium thiosulfate[4].

Manganese, if present, may be partially oxidized in ammoniacal solution, causing the liberation of additional iodine upon the addition of potassium iodide. This may be prevented by adding the bifluoride before the ammonium hydroxide to keep the solution acidic throughout the procedure[29, 80].

The precipitated cuprous iodide absorbs some of the liberated iodine[47], causing the end point to be rather unsatisfactory and also making the method empirical since the end point appears before the equivalence point is reached. Foote and Vance[41] suggested the addition of 2 to 3 grams of ammonium thiocyanate just before reaching the end point in the titration, and this modification has been adopted quite widely. At least part of the cuprous iodide is transformed to cuprous thiocyanate, which does not adsorb the small amount of iodine present at this point.

It is best to remove most of the nitric acid by evaporation or by adding sulfuric acid and fuming, if the thiocyanate is to be added. Fuming with sulfuric acid may cause a partial reduction of arsenic or antimony and therefore should be followed by a bromine-water treatment. If the titration is made in buffered sulfate-hydrogen sulfate solution, several milliliters of concentrated nitric acid may be present[47].

In place of ammonium thiocyanate, the corresponding sodium or potassium salt may be used. Hammock and Swift[47] prefer the potassium salt since extensive decomposition was found in different lots of ammonium thiocyanate.

It should be emphasized that if the thiocyanate is not used, the thiosulfate solution should be standardized with pure copper under the same conditions that are to be used later.

A rapid method for decomposing sulfide ores directly with 70 per cent perchloric acid has been developed by Goetz, Diehl, and Hach[45], which requires only five minutes for complete decomposition and yields a solution containing the elements in their higher states of oxidation. The iodometric procedure may be applied directly to this solution.

Thiocyanate Methods. After separating cuprous thiocyanate as discussed under Separation, it may be titrated with permanganate[32, 46, 79] or potassium iodate under various conditions. An advantage is that molybdenum does not interfere. The permanganate methods are empirical, but the iodate methods are quite generally satisfactory. In one iodate procedure[52] the cuprous thiocyanate is dissolved in hydrochloric acid, some chloroform added, and standard iodate solution added until the violet iodine color disappears from the chloroform layer.

$$4CuCNS + 7KIO_3 + 14HCl \rightarrow 4CuSO_4 + 7ICl + 4HCN + 7KCl + 5H_2O$$

In another modification[20] an excess of the standard iodate solution is added to the hydrochloric acid solution of the cuprous thiocyanate. Then, upon the addition of potassium iodide, iodine is liberated from the iodine monochloride formed in the first reaction as well as from the excess iodate. The liberated iodine is titrated with standard sodium thiosulfate solution using starch indicator.

$$ICl + KI \rightarrow I_2 + KCl$$

$$KIO_3 + 5KI + 6HCl \rightarrow 3I_2 + 6KCl + 3H_2O$$

and

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

It is also possible to precipitate cuprous thiocyanate with an excess of standard thiocyanate solution and back-titrate the excess with standard iodate solution potentiometrically[49].

Cupric copper may be reduced with hydroxylamine sulfate and titrated with thiocyanate in an inert atmosphere using a ferric salt as indicator, although the results are usually slightly low[53].

Reduction Methods. In 2*M* hydrochloric acid solution cupric ion is reduced quantitatively to the cuprous state by the silver reductor. Birnbaum and Edmonds[15] collect the reduced solution in ferric alum solution and titrate the resulting ferrous ion with ceric sulfate. Nitric acid, zinc, tin, arsenate, bismuth, and cadmium do not interfere, but iron, molybdenum, uranium, and vanadium must be absent.

Cupric copper in 4 to 6*N* hydrochloric acid solution may be titrated potentiometrically with standard chromous sulfate solution[60] in a carbon dioxide atmosphere. A very sharp change in potential is obtained upon reduction to the cuprous state and a much smaller change upon reduction to metallic copper[105]. Lingane and Auerbach[59] utilize the first sharp break to determine copper in antimony-tin-copper alloys.

Titanous sulfate or chloride solutions may be used to titrate cupric ion to the cuprous state. Thornton[93] has reviewed the various modifications of this method; several more recent variations have appeared[36, 106].

Vanadous (V^{++}) solutions reduce cupric ion to the metal. An excess of standard vanadous solution may be added and the excess back-titrated[100].

It has been reported that copper may be determined by reducing it to the cuprous state with bismuth amalgam, adding an excess of ferric alum and titrating the ferrous ion formed with standard ammonium vanadate solution using *N*-phenylanthranilic acid as indicator[92].

Cyanide Method. The cyanide method depends upon the reaction of the blue cupric ammonia complex ion with potassium cyanide to form a negative complex of cuprous copper and cyanide, which is colorless[86].

$$2Cu(NH_3)_4(NO_3)_2 + 7KCN + H_2O \rightarrow K_4Cu_2(CN)_6 + NH_4CNO + \\ 3KNO_3 + NH_4NO_3 + 6NH_3$$

The method is not particularly accurate and is highly empirical. Silver, nickel, cobalt, cadmium, and zinc interfere.

Miscellaneous Volumetric Methods. McDowell and Johnston[69] suggest *the potentiometric titration of cupric copper with a standard ferrocyanide* solution. They claim accurate results for low concentrations of copper, down to 1 × 10^{-6} *M*, but show no results.

Cupric ion may be titrated conductometrically with a standard solution of cupferron. The method determines copper in brass without removing lead or tin[25].

Colorimetric (Photometric) Methods

Many colorimetric methods for the determination of small amounts of copper are found in the literature[95]. Snell and Snell[91] give details for most of them, including preparation of the sample, procedures, and literature references through 1947.

The method chosen will depend upon the amount of copper to be determined, since there is considerable variation in sensitivity among the various acceptable procedures. Müller and Burtsell[71] make some interesting comparisons of relative sensitivities for a number of them. The method of color comparison (Nessler tubes, photoelectric colorimeter, etc.) to be used will determine the range of copper concentrations over which the reagent is useful. In the following discussion the ranges are approximate and serve mainly to show the relative sensitivities.

Undoubtedly the most widely used method is the diethyldithiocarbamate procedure in which the sodium salt of the reagent is added to the ammoniacal solution of cupric copper to give an orange-brown dispersion of the copper salt of diethyldithiocarbamate. The final solution should contain 0.05 to 0.15 mg of copper per 100 ml. The transmittancy of the stabilized aqueous dispersion may be determined, or preferably the copper compound is extracted with chloroform, carbon tetrachloride, amyl alcohol, amyl acetate, or bromobenzene and the transmittancy of the organic liquid phase determined.

The list of interferences is quite imposing and includes aluminum, antimony, bismuth, cadmium, chromium, cobalt, iron, lead, molybdenum, manganese, mercury, nickel, silver, tin, titanium, uranium, vanadium, tungsten, and zinc[55]. However, many of these substances do not interfere when present in moderate amounts. The addition of citrate and the use of the extraction eliminate the difficulty with iron.

The diethyldithiocarbamate method has been adopted by the American Public Health Association[3] for the determination of copper in water and by the Association of Official Agricultural Chemists[11] for copper in plant materials.

A reagent prepared from carbon disulfide and diethanolamine reacts with cupric ion to form a brownish-yellow salt of bis(2-hydroxyethyl)-dithiocarbamic acid, which is soluble in water and does not require stabilization or extraction[44, 99].

The most sensitive method is the diphenylthiocarbazone (dithizone) method, which is limited to the determination of 0.001 to 0.05 mg of copper. A carbon tetrachloride solution of dithizone gives a red-violet copper complex which is extracted into the carbon tetrachloride layer if the acidity of the aqueous phase is 0.1*N* or less. The transmittancy of the carbon tetrachloride layer, which also contains the excess dithizone (green), is best determined with a green filter or monochromatic light with a wave length of 510 mμ. Palladium, gold, silver, mercury, bismuth, and ferric iron interfere. This is an extremely useful procedure for the determination of traces of copper in all types of material, and Sandell[84] gives excellent directions for these applications.

The olive green color obtained upon adding rubeanic acid (dithio-oxamide) to a weakly acid solution of cupric ion is useful for the determination of 0.05 to 0.2 mg of copper. It has been applied to ores, steel[70], magnesium alloys[91, 98], etc. West and Compere[97] recommend its use along with malonic acid for the rapid determination of copper in water.

In concentrated hydrobromic acid solution, cupric compounds give a violet color, which is the basis for the determination of 0.02 to 0.25 mg of copper. This method has been adopted by the American Society for Testing Materials for determining copper in aluminum alloys, antimony metal, lead metal, and bearing metal[8].

The addition of a soluble ferrocyanide to a dilute acetic acid solution of copper yields a reddish-brown dispersion of cupric ferrocyanide. As a colorimetric method, this reaction is most useful for 0.05 to 5 mg of copper.

The brown coloration due to a colloidal dispersion of cupric sulfide has long been used as a means of determining small amounts of copper remaining in solution after electrodeposition. As much as several tenths of a milligram of copper may be determined with hydrogen sulfide. The method may be extended to several milligrams of copper if the dispersion is stabilized with gelatin.

The addition of ammonium hydroxide to a cupric salt solution yields the deep blue color of the cupric ammonia complex ion. This reaction is not particularly sensitive and therefore is suitable for the determination of considerably higher concentrations of copper than is possible with the reactions previously described. The final solution may contain as much as 100 mg of copper per 100 ml. The sensitivity may be increased somewhat by substituting triethanolamine or tetraethylenepentamine for the ammonium hydroxide.

Alpha-benzoinoxime may be used to precipitate copper from an alkaline tartrate solution; the cupric salt may then be extracted with chloroform and determined photometrically[35].

The use of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline offers the possibility of a highly specific method for the colorimetric determination of copper[90a].

2,2′-biquinoline appears to hold promise as a color reagent for copper, since as little as 0.02 microgram of copper per milliliter can be determined[50].

Determination of Metallic Copper, Cuprous Oxide, and Cupric Oxide in Mixtures

Cuprous oxide may be dissolved from a mixture of cuprous oxide, cupric oxide, and metallic copper by ammonium hydroxide or hydrochloric acid solution in the presence of hydrazine sulfate and in an atmosphere of carbon dioxide. The residue of copper and cupric oxide may be isolated and the metal determined by direct solution in acid ferric chloride, followed by titration of the resulting ferrous ion with standard dichromate or ceric sulfate solution[12, 13, 51, 103]. A statistical counting method under the microscope may also be employed[104].

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